This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

311
M3

UC-NRLF
$B 50 841

YC 40025

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

Cambridge Engineering Tracts

General Editor
B. HOPKINSON, M.A.

No. 2

THE LAWS OF THERMODYNAMICS

by

W. H. MACAULAY, M.A.
Fellow of King's College, Cambridge

Cambridge University Press
C. F. Clay, Manager
London: Fetter Lane, E.C.
Edinburgh: 100, Princes Street
1913

Price 3s. net

Digitized by Google

Digitized by Google

Cambridge Engineering Tracts

General Editor
B. HOPKINSON, M.A.

No. 2

The Laws of Thermodynamics

Digitized by Google

CAMBRIDGE UNIVERSITY PRESS
London: FETTER LANE, E.C.
C. F. CLAY, MANAGER

Edinburgh: 100, PRINCES STREET
Berlin: A. ASHER AND CO.
Leipzig: F. A. BROCKHAUS
New York: G. P. PUTNAM'S SONS
Bombay and Calcutta: MACMILLAN AND CO., LTD.

All rights reserved

Digitized by Google

THE LAWS OF THERMODYNAMICS

by

W. H. MACAULAY, M.A.
Fellow of King's College, Cambridge

Cambridge:
at the University Press
1913

Digitized by Google

QC 311
M3

Cambridge:
PRINTED BY JOHN CLAY, M.A.
AT THE UNIVERSITY PRESS

Digitized by Google

PREFACE

THE aim of this tract is to provide a connected and accurate account of the fundamental principles of thermodynamics, combined with a sketch of methods of applying the theory in special cases, to supplement technical books on the subject. It may be well to warn a beginner not to attempt to read it straight through, but rather to use it as a help, in conjunction with other information.

345080

Digitized by Google

Digitized by Google

CONTENTS

Chapter I. Functions of two variables.

SECT.		PAGE
1.	Introductory	1
2.	Diagrams	1
3.	Line integrals	1
4.	Perfect differentials	2
5.	$Mdx+Ndy$ when not a perfect differential	6

Chapter II. The first law of thermodynamics.

6.	Measurement of heat	8
7.	Temperature	9
8.	The first law of thermodynamics	10
9.	The energy equation	12
10.	Combustion of fuel	13
11.	Internal combustion engine	14
12.	Continuous reversible processes	15
13.	Adiabatic processes	18
14.	Fluid working substance	19

Chapter III. Particular types of substance.

15.	A vapour and its liquid	21
16.	Superheated vapour	23
17.	$E+Apv$	23
18.	Throttled vapour	25
19.	Perfect gas	27

Chapter IV. The second law of thermodynamics.

20.	Introductory	33
21.	Example of apparatus for transferring heat	34
22.	Carnot's engine	35
23.	Carnot cycle	38
24.	Thermodynamic scale of temperature	39
25.	Any reversible process	40
26.	Historical note	42

Digitized by Google

Chapter V. Entropy.

SECT.		PAGE
27.	Definition of entropy	45
28.	Irreversible processes	46
29.	Equations for reversible processes	49
30.	A vapour and its liquid	50
31.	Cycle with irreversible step	54
32.	Thermodynamic relations	55
33.	Characteristic equations and specific heats	57
34.	Electromotive force of a storage battery	60

Chapter VI. Entropy of a system.

35.	Entropy of a system	64
36.	Availability of heat	66

Chapter VII. Any number of independent variables.

37.	Generalisation of the theory	69

Digitized by Google

CHAPTER I

FUNCTIONS OF TWO VARIABLES

1. The fundamental propositions of the theory of Thermodynamics involve the consideration of variations in the state of a substance, when its state is specified by the values of two quantities which may vary independently. Thus some attention must be paid to the mathematical theory of functions of two variables, and the following account of some points in the theory may be useful for reference.

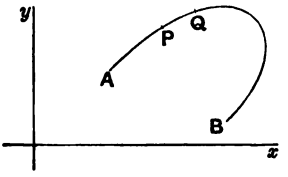
2. Diagrams. Let x and y be two variable quantities capable of assuming either any real values, or any that lie within some given range. If they represent physical quantities they may have some necessary limits of range implied in their definitions; or there may be practical reasons for limiting the range of values which they are permitted to have. Variations of x and y may be shewn by a diagram in which they are used as rectangular coordinates. If the range of values of x and y is limited, the area of the diagram has corresponding limits. Any pair of values of x and y is represented in the diagram by a point. Any process which is specified by a certain continuous change in the values of x and y is represented in the diagram by a continuous line. It may also be represented by an equation connecting x and y; or part of the line may happen to be represented by one equation, and part of it by a different one.

3. Line integrals. It is often convenient to specify an integral involving x and y by reference to a line in the diagram. Let M be a given function of x and y, with a single finite value at each point of the diagram, and varying continuously from point to point; and let AB be a given line. Then "$\int M dx$ along the line AB" is to be interpreted in the following manner.

Suppose the line AB to be traversed from A to B by successive steps, and for each step PQ take the value of M at P, and the increment of x, namely δx, for the step from P to Q; then the

Digitized by Google

integral is the limit of the sum of all the products $M\delta x$ when the steps are infinitesimal*. Thus $\int M dx$ along the line AB is equal to $-\int M dx$ along the line BA. Let N be another continuous function of x and y, with a single finite value at each point; then $\int N dy$ and $\int (M dx + N dy)$ along a line AB are to be similarly interpreted.



The value of $\int y dx$ along a line AB is represented in the diagram by an area; for it is equal to the area swept out by the ordinate of a point as it traverses the line from A to B, portions of area swept out as x increases being reckoned positive, and portions swept out as x is decreasing being reckoned negative. Thus it is equal to the algebraical sum of certain areas which may be shewn in a diagram, of which some may be positive and some negative, and some may overlap. If the line is closed, A and B coinciding, it is equal to the area enclosed by the line, provided that this is reckoned positive if the circuit is traversed one way round, and negative if it is traversed the other way round. If, according to the usual practice, the coordinate axes are drawn so that the axis of y points north when the axis of x points east, an area is to be reckoned positive when its circuit is traversed clockwise. If the circuit intersects itself the integral is equal to the algebraical sum of portions of area, with signs attached to them according to this rule†. It is clear that $\int y dx$ along any closed circuit is equal to $-\int x dy$ along the same circuit.

4. Perfect differentials. It is clear that, in general, the value of $\int (M dx + N dy)$ along a line AB depends not only on the positions of the initial and final points A and B, but also on the form of the line, or what may be called the route from A to B. But there are exceptional cases of integrals, of this type, such that their values depend only on the positions of the initial and final points, and are independent of the route. These are cases in which $M dx + N dy$ happens to be the differential of some quantity which is a function of x and y. The

* The definition of the integral applies to cases in which the value of M undergoes abrupt change at a definite number of points as the line is traversed.

† If x and y are respectively the volume and pressure of the contents of the cylinder of an engine, an indicator diagram shews their variations, and its area represents the work done by the engine; and if a loop occurs in the diagram, the area of the loop denotes negative work.

Digitized by Google

integral is then equal to the increase of this quantity due to the passage from A to B. For example, take $\int(xy^2dx+x^2ydy)$; here $Mdx+Ndy$ may be written $d(\frac{1}{2}x^2y^2)$, therefore the value of the integral along any line from a point x_1, y_1 to a point x_2, y_2 is simply $\frac{1}{2}x_2^2y_2^2-\frac{1}{2}x_1^2y_1^2$, whatever route is adopted.

To deal with the question in an orderly way, let us approach it from a different point of view. Let M and N be such that $\int(Mdx+Ndy)$ along a line from any one point of the diagram to any other point has the same value for all routes; and let ϕ be a function of x and y defined as follows. Choose a point A in the diagram, and give ϕ an arbitrarily chosen value, ϕ_A, at this point, and let its value, ϕ_P, at any other point P be

$$\phi_A+\int(Mdx+Ndy) \text{ along a line from } A \text{ to } P.$$

Thus ϕ has a definite value at each point of the diagram, given by the value of the integral along a line which starts from A.

$$\int(Mdx+Ndy) \text{ from } A \text{ to } P=\phi_P-\phi_A,$$

and

$$\int(Mdx+Ndy) \text{ from } P \text{ to } A=\phi_A-\phi_P.$$

The value of the integral between any two points in the diagram can then be specified in terms of ϕ; in fact the scheme is the same as that which is adopted when differences of level of places on a map are specified by marking on the map the height of each place above some arbitrarily chosen datum level. The value of the integral from any point P to any other point Q, being the same for all routes from P to Q, may be found by taking a route passing through A; so it is equal to the value of the integral from P to A plus its value from A to Q, that is to say it is $\phi_Q-\phi_P$. Thus for an elementary step, $Mdx+Ndy$ may be written $d\phi$, or $\frac{d\phi}{dx}dx+\frac{d\phi}{dy}dy$. Therefore M and N must be the partial differential coefficients of ϕ with regard to x and y respectively, and must satisfy the equation

$$\frac{dM}{dy}=\frac{dN}{dx}.$$

If all that is given is that M and N satisfy this equation, $\frac{dM}{dy}=\frac{dN}{dx}$, a function of x and y exists of which $Mdx+Ndy$ is the differential, as will be shewn below, and $Mdx+Ndy$ is said to be a perfect differential. But it is not certain that the function may

Digitized by Google

not, like $\tan^{-1}\frac{y}{x}$, have more than one possible value at each point of the diagram. It will, however, be shewn that the integral between two given points has the same value for any two routes, provided that these routes do not enclose between them any points at which the conditions stipulated for the diagram are violated.

The following are examples of expressions, of the form $M\,dx + N\,dy$, which are the differentials of functions of x and y:

$$y\,dx + x\,dy, \quad 2xy\,dx + x^2dy, \quad \sin y\,dx + x\cos y\,dy;$$

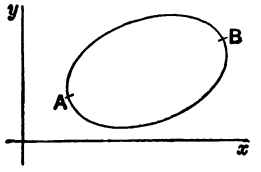
the functions being xy, x^2y, and $x\sin y$ respectively. In each case $\frac{dM}{dy}$ and $\frac{dN}{dx}$ are identical, and the value of $\int(M\,dx + N\,dy)$ between two given points is independent of the route.

The following are examples of expressions, of the form $M\,dx + N\,dy$, which do not possess the property of being perfect differentials:

$$y\,dx, \quad 2y\,dx - x\,dy, \quad (x^2 - y^2)\,dx + 2xy\,dy.$$

In such cases the value of $\int(M\,dx + N\,dy)$ between two given points depends on the route, and $\frac{dM}{dy}$ is not equal to $\frac{dN}{dx}$.

If $\int(M\,dx + N\,dy)$ is such that its value between any two points is independent of the route, the value of it along a closed circuit is zero. For if A and B are two points on a circuit, there are two different routes from A to B along the line, and $\int(M\,dx + N\,dy)$ from A to B by one route is equal to $-\int(M\,dx + N\,dy)$ from B to A by that route, and therefore also by the other route.



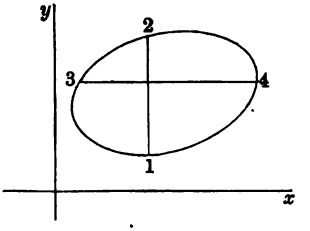
The relation between the value of $\int(M\,dx + N\,dy)$ for a circuit and values of $\frac{dM}{dy} - \frac{dN}{dx}$ at points of the diagram is exhibited by the following investigation.

Take a circuit enclosing a single area over which M and N are finite and continuous. Then $\int\frac{dM}{dy}\,dy$ along a line 12 parallel to the axis of y, and bounded by the circuit, is equal to $M_2 - M_1$*;

* This procedure may be arranged so as to provide for cases in which some of the lines parallel to the axes cut the circuit more than twice.

Digitized by Google

therefore $\iint \frac{dM}{dy}\,dx\,dy$ over the area bounded by the circuit is equal to $\int M\,dx$ along the circuit clockwise. Similarly $\int \frac{dN}{dx}\,dx$ along a line 34 parallel to the axis of x, and bounded by the circuit, is equal to $N_4 - N_3$; therefore $\iint \frac{dN}{dx}\,dx\,dy$ over the area is equal to $-\int N\,dy$ along the circuit clockwise. Therefore $\iint \left(\frac{dM}{dy} - \frac{dN}{dx}\right) dx\,dy$ over the area is equal to $\int (M\,dx + N\,dy)$ along the circuit clockwise. Accordingly, if $\frac{dM}{dy} - \frac{dN}{dx}$ is zero at every point of the area, $\int (M\,dx + N\,dy)$ along the circuit is zero; so that the values of this integral for alternative routes which enclose this area are equal. If M or N were infinite or discontinuous at any points enclosed by the circuit, the integration over the area would be invalid.



If M and N are such that $\frac{dM}{dy} = \frac{dN}{dx}$, a quantity, ϕ, can be found of which $M\,dx + N\,dy$ is the differential, in the following manner. What is required is that $\frac{d\phi}{dx}$ and $\frac{d\phi}{dy}$ should be respectively M and N, which are supposed to be given functions of x and y. Let a function ψ be found such that $\frac{d\psi}{dx} = M$. Then

$$\frac{d^2\psi}{dx\,dy} = \frac{dM}{dy} = \frac{dN}{dx},$$

therefore $N = \frac{d\psi}{dy}$ + a function of y only. This function is known since N and $\frac{d\psi}{dy}$ are both known; write it in the form $\frac{d\chi}{dy}$, where χ is a function of y only. Then $\psi + \chi$ is the function of x and y which we are seeking.

For example, suppose M and N to be $2xy$ and $x^2 + y + 1$ respectively. Then x^2y will do for ψ; and $N = \frac{d\psi}{dy} + y + 1$, so that $\frac{1}{2}y^2 + y$ will do for χ. Thus $x^2y + \frac{1}{2}y^2 + y$ is the required function whose differential is $M\,dx + N\,dy$.

Digitized by Google

5. $Mdx+Ndy$ when not a perfect differential. It can be proved that if M and N have differential coefficients, but not such that $\frac{dM}{dy}$ and $\frac{dN}{dx}$ are equal, a factor μ can always be found such that $\mu Mdx+\mu Ndy$ is the differential of some function of x and y, say ϕ; so that $Mdx+Ndy=\frac{1}{\mu}d\phi$. For example

$$2ydx-xdy=\frac{y^2}{x}d\left(\frac{x^2}{y}\right),$$

and
$$(x^2-y^2)dx+2xydy=-(x^2+y^2)^2 d\left(\frac{x}{x^2+y^2}\right).$$

Thus, whether $Mdx+Ndy$ is a perfect differential or not, the differential equation

$$Mdx+Ndy=0$$

(except so far as it is satisfied by $\frac{1}{\mu}=0$) is equivalent to $\phi=C$, where C is a constant. This equation is represented in the diagram by a system of curves, distinguished from one another by the value chosen for C. The differential equation may also be regarded as specifying a variation of x and y by the motion of a point travelling with given steering directions, the slope of its path at any point being the value of $-\frac{M}{N}$ at that point. We have a single definite slope at each point of the diagram, except possibly at points at which M and N are simultaneously zero. Thus the curves fill the diagram, and no two of them can intersect, except possibly at points at which M and N are simultaneously zero.

Any number of the curves may be drawn on the diagram, and intermediate ones imagined. If they are interpreted as contour lines on a map, ϕ may be interpreted as representing the height of the ground at the point x, y. In general, starting from any given point 1 with coordinates x_1, y_1, a single contour line is found passing through it, namely the line for which C has the value ϕ_1; and variations of x and y in accordance with the equation $Mdx+Ndy=0$ are given by following this line.

A given differential equation of the form

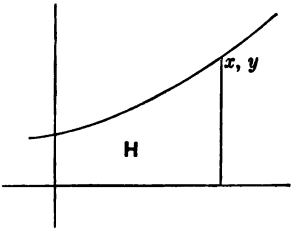
$$Mdx+Ndy=0$$

specifies only the contour lines for a surface representing ϕ; and by taking different arrangements of intervals of height between the lines

Digitized by Google

we may construct any number of different surfaces. Any particular expression that is found for ϕ in terms of x and y is represented by some one of these surfaces. In fact, if the differential equation is equivalent to the statement that ϕ is constant, it is equally equivalent to the statement that ϕ^2, or any other function of ϕ, is constant. If one of the surfaces represents a certain expression ϕ, the others represent respectively all possible functions of ϕ.

Let H be a quantity such that $dH = Mdx + Ndy$, although $\frac{dM}{dy} - \frac{dN}{dx}$ is not zero. Then H has a definite increment, dH, corresponding to given infinitesimal increments of x and y, but it is not a function of x and y. As an example of this, let H be the area between a curve and coordinate axes and the ordinate at the point x, y. Then dH is equal to ydx whatever the curve may be; but H depends not only on the values of x and y, but also on the form of the curve. A similar geometrical illustration is given by $dH = -ydx + xdy$.



In all such cases, if x and y represent physical quantities specifying the state of some physical system, H represents a quantity depending not only on the state of the system at any given instant, but also upon its past history. It is related to some process which the system is undergoing, and if its values are to be determined the process must be fully specified. Quantities of this character, such as the amount of work done, or the quantity of heat received by the system, as it passes from one state to another, must be distinguished from such quantities as volume, temperature, energy, or entropy, which can be determined from mere examination of the state of the system, without account being taken of any process that it is undergoing.

Digitized by Google

CHAPTER II

THE FIRST LAW OF THERMODYNAMICS

6. Measurement of heat. A quantity of heat means the measure, given by a calorimeter, of what a body receives or parts with in one or other of two recognisable operations, namely conduction of heat and radiation of heat. The standard unit quantity of heat, adopted by physicists for this measurement, is that which, when received by a gramme of water, raises its temperature one degree centigrade at the temperature 15° C., that is to say practically from $14\frac{1}{2}$° C. to $15\frac{1}{2}$° C. This is called a calorie. The same quantity parted with by a gramme of water at $15\frac{1}{2}$° reduces its temperature to $14\frac{1}{2}$°. Two calories means the quantity of heat which produces this change in two grammes of water, and so on. The more general term "thermal unit" will be used to denote either the calorie or any other unit quantity which is defined in the same way, but with a different unit mass of water, or a different interval of temperature. It is hardly necessary to take account of any alternative to the centigrade division of the temperature scale, and the interval of temperature chosen for the calorie; but engineers often use a thermal unit which is given by substituting some other unit of mass, a pound or a kilogramme, for a gramme. In the latter case the unit is 1000 calories. This variation of usage is not seriously inconvenient, as numbers denoting heat per unit mass of a substance are not affected by it. The use of the calorie, or other thermal unit, is not confined to cases in which there is an actual quantity of heat to be measured; for the first law of thermodynamics justifies an extension of the use of it to the measurement of any quantity of energy, as an alternative to the use of a work unit.

If receiving of heat by one body is directly associated with parting with heat by another body, the two quantities are equal, and the operation is correctly described as a transfer of heat.

The quantity of heat received by a body is usually denoted by an

Digitized by Google

algebraical quantity, which may be either positive or negative, a negative quantity of heat received denoting heat parted with. If we are concerned only with heat passing between bodies of a given system, the algebraical sum of the quantities of heat received by the various bodies is zero.

It should be noted that a quantity of heat always has reference, direct or indirect, to a process in which heat is received or parted with; and that it is not possible to say that a body possesses or contains a certain quantity of heat*.

7. Temperature. The distinction between higher and lower temperatures is based on the fact that, if two portions of matter of different temperatures are in contact, a transfer of heat takes place between them from that which has the higher to that which has the lower temperature. Any number of bodies, whose temperatures differ, can be arranged in order of temperature in only one way; thus the temperature of a body may be given a numerical value derived from its position in this order.

The scale of temperature which is used in the theory of heat is what is called the thermodynamic scale, or the absolute scale. This is an absolute scale in the sense of not being based on the special properties of any particular substance; but it is defined (p. 39) in a way which provides for its approximate agreement with the scales defined by gas thermometers. The scale of the constant volume hydrogen thermometer, in which increments of temperature are measured by increments of pressure, is practically referred to as the standard scale for a considerable range of temperature. The divergences of this scale from the absolute scale are negligible in practical measurements of temperature†.

* Such a statement as this would be somewhat analogous to saying that a certain lake contains a certain quantity of rain. Water ceases to be rain as soon as it has fallen; and no examination of a lake now and a week ago could reveal the quantity of rain which fell into it during the past week, because a lake receives and parts with water in other ways, by means of streams running into and out of it, and by evaporation. Yet rainfall may be measured by effects produced if suitable precautions are taken, that is to say by means of a rain gauge.

† With the standard pressure that is adopted for the constant volume hydrogen thermometer, namely that of 1000 mm. of mercury at 0° C., the greatest divergence from the absolute scale between the fixed points 0° and 100° C. is about 0·001°; the greatest divergence between −100° and 300° occurs at each of these two limits, and is about 0·01°; and the divergence at −200° is about 0·06°. (*Kaye and Laby's Tables of Physical and Chemical constants*, 1911, p. 44.)

Digitized by Google

The centigrade division of the scale gives 100 units, or degrees, between the temperature of melting ice and that of boiling water, at a pressure of 760 mm. of mercury in latitude 45°. All scales are arranged to agree at these two temperatures, which are called the fixed points. The former of these temperatures is the ordinary zero which is generally used for the quotation of observed temperatures. It would however be inconvenient to use for the purpose of theoretical equations a zero depending on the properties of water. A different zero point, called the absolute zero, is used for this purpose. It is defined by the formula on which the thermodynamic scale is based, and is very nearly identical with what may be called the absolute zero point of the hydrogen thermometer. This is a point such that the temperature reckoned from it on the hydrogen thermometer scale is proportional to the pressure of the hydrogen.

The absolute zero is about 273° C. (more nearly 273·1°) below the ordinary zero. Temperatures reckoned from this point are called absolute temperatures. Two different symbols might be used for the two values of a temperature, reckoned respectively from the absolute zero and from the ordinary zero; but this need not be done, as a doubt about which zero is employed in any particular case does not often occur in practice.

8. The first law of thermodynamics. The general theory of Thermodynamics, apart from the special properties of particular substances, is contained in two laws, called respectively the first and the second law of thermodynamics. The theory was formulated about the year 1850. The first law, as an exact result, was based mainly on Joule's experimental work of the previous decade. The second law served to embody, in the new theory, Carnot's theory of the efficiency of heat engines, which had been published by him in 1824; it deals with the position which temperature holds in the theory.

The first law of thermodynamics is that, when a body receives or parts with heat, it receives or parts with energy; and that the quantity of energy, measured by mechanical work, bears a fixed proportion to the quantity of heat measured in thermal units. The number expressing the work value of a thermal unit is called the mechanical equivalent of heat, or Joule's equivalent, and is denoted by J. If the thermal unit is that derived from one pound of water and the centigrade degree of temperature, and a foot-pound is taken as the unit of work or energy, the value of J is about 1400. This number corresponds to

Digitized by Google

$4{\cdot}185 \times 10^7$ ergs to a calorie. Thus we may use the same unit for measuring both heat and work, expressing heat in work units or work in thermal units, as may be most convenient.

Joule's work had practically the effect of establishing the principle of conservation of energy. For one thing, it shewed for the first time by accurate measurement that it was possible to account for the work lost by friction, in ordinary mechanics, in the form of a gain of energy by the bodies concerned. It was recognised that any body (including under this term any material system), in a given condition, possesses a certain stock of energy, any change in which can be traced as a passage of a certain measurable quantity of energy to or from it; and that the amount of energy possessed by the body is a function of the quantities which specify its condition, so that if it undergoes a complete cycle of changes, returning to its initial condition, the net amount of energy received by it during these changes is zero.

The energy here regarded as possessed by a body does not include potential energy due to actions between it and some external system. The body may possess kinetic energy as reckoned in ordinary mechanics. The remainder of its stock of energy is called its Internal (or Intrinsic) Energy.

It may be supposed that some of the internal energy of a body might be reckoned as kinetic energy of molecular motion. But it is not necessary for our present purpose to enquire into this. Accordingly the term kinetic energy, used without qualification, means here the kinetic energy of which account is taken in ordinary mechanics. If it is necessary to distinguish this from energy of molecular motion, it will be called the kinetic energy of sensible motion. Sensible motions are motions which can be identified and traced in detail by direct observation. Molecular motions cannot be traced by direct observation, or manipulated individually, and are recognised by their aggregate effects, such as are specified by temperature or pressure. The distinction is a real and important one. We have good reasons for believing that, if molecular motions could be manipulated individually, the second law of thermodynamics would not be true.

Sensible motions of bodies, relative to a suitable base, can be manipulated by suitable guidance so as to yield mechanical work at the expense of the energy which they represent. Some of the internal energy of a body may be represented by motions which are so organised as to yield mechanical work under suitable conditions; but no means exist for applying individual guidance to molecular

Digitized by Google

motions to complete such organisation. Thus we may expect a limit to be imposed on the availability of energy of molecular motions for production of useful work, which does not apply to sensible motions. The ordinary rules for the calculation of the kinetic energy of a system would justify a division of it into two parts, such as is here suggested.

We have no knowledge of the total value of the internal energy of any body, and any value assigned to it must be understood to be the amount by which the internal energy of the body, in the state which is under consideration, exceeds that which it possesses in some standard state. It is convenient to suppose the standard state to be so chosen that negative values for the energy do not occur; otherwise the choice is unimportant.

9. The energy equation. If any body, or material system, receives a quantity of heat Q while it does mechanical work W*, driving some external system, and does not receive or part with energy in any other way, the energy equation, expressing the first law of thermodynamics, is

$$Q = E_2 - E_1 + W,$$

where E_1 is the energy of the system at the beginning of the operation, and E_2 its energy at the end of it. In this equation the same unit must be used for heat and work. Here Q and W are algebraical quantities representing the net amount of heat received, and the net amount of work done during the operation; negative work being work done upon the system by some external source of power. The case of friction between the system in question and an external body is not provided for by this equation. This is a case of a certain amount of energy being divided between the system and the external body in a proportion not generally known. It may however be practicable to estimate it and take account of it in particular cases.

Take, as an illustration of this equation, the type of experiment employed by Joule, in which a measured amount of work is applied to stir a fluid by means of paddles, the apparatus being carefully guarded from receiving or parting with heat. The work done is equal to the increase of energy of the apparatus (fluid and paddles and vessel containing them) which, when the fluid has come to rest, is marked by an increase of temperature. The apparatus might then be brought

* The theory may be extended to cases in which energy leaving or entering the system in certain stated ways, other than by mechanical work or passage of heat, is included in W; thus electrical work may be included if necessary.

Digitized by Google

back to its initial state by allowing it to part with heat. Thus work may be said to be converted into heat, whose energy value is equal to the work expended. The actual procedure in an experiment is to measure the rise of temperature, and to calculate the quantity of heat which would produce this rise of temperature from the specific heat of the fluid, and of the rest of the apparatus, obtained independently.

The operation of raising the temperature of a body by communication of heat to it is a reversible one, for the body can part with the same quantity of heat, its temperature being restored to its original value if the process is in all respects reversed. But the operation of raising the temperature of a fluid by stirring it, which involves friction, is irreversible; the conversion of heat into mechanical work by a reversal of the whole process described above is not possible.

10. Combustion of fuel. A furnace is an apparatus for supplying heat at the expense of the internal energy of the substance with which it is fed, namely fuel and air. The amount of mechanical work done by expansion of the substance is unimportant, and the quantity of heat supplied is practically the excess of the energy of the substance as it enters the furnace over that carried away by the products of combustion. The fuel and oxygen involved in the chemical change which takes place is only a certain proportion of the substance; the greater part of it, including some of the oxygen and all the nitrogen of the air, acts as a vehicle of heat, besides having its temperature raised. The quantity of heat obtained from a furnace, per unit mass of fuel, depends on the calorific value of the fuel, the quantity of air used, the completeness of the combustion, and the temperature of the products of combustion. Combustion is regarded as complete when the carbon and hydrogen of the fuel are burnt to carbon dioxide and water or steam. In an actual furnace it is to some extent incomplete.

The calorific value of the fuel is determined by a laboratory test performed so as to secure complete combustion, the heat parted with being measured by a calorimeter. To give an exact meaning to the result thus obtained, the conditions of the test, including the initial and final states of the substance, must be specified. The calorific value of a given fuel means the quantity of heat which is parted with, per unit mass of the fuel, when the test is conducted at constant volume, so that no work is done, and the temperature of the products of combustion is the same as that of the fuel and oxygen before

Digitized by Google

combustion. This temperature is usually such that most of the steam that is formed is condensed. The quantity of heat evolved if the steam is all condensed is called the higher calorific value of the fuel. The lower calorific value may be calculated from the higher calorific value, or may be determined independently. It means the quantity of heat produced when the cooling of the products of combustion is only carried to the point at which the steam has just not begun to condense. Neither of these terms has a quite precise meaning, because the initial temperature of the fuel and oxygen is not specified.

The quantity of heat supplied by a furnace may be known from effects produced, such as the evaporation of water when the heat is supplied to a boiler; or it may be estimated from the quantities of fuel and air used, the calorific value of the fuel, and the temperature and composition of the products of combustion. An allowance for any carbon monoxide present in the products of combustion may be made, if necessary, by means of chemical data. The efficiency of a furnace is defined as meaning the ratio of the quantity of heat which it supplies, per unit mass of fuel, to the calorific value of the fuel, usually the lower value.

11. Internal combustion engine. The object of the combustion which takes place in the cylinder of an internal combustion engine is to produce work from internal energy. The working substance of the engines in practical use is air combined with a small proportion of fuel. The fuel is generally gaseous, but it may be liquid, and it might even be solid dust. Carnot, writing in 1824, mentions the experimental use of fuel consisting of the fine dust called lycopodium, injected into the air. Carnot approached the subject, not from the point of view of explosion, as some pioneers did, but from the point of view of the practical difficulty of communicating heat to air effectively and rapidly, and the consequent obstacles to the employment of air as the working substance of an engine. He pointed out the advantages of using air with internal combustion, if practical difficulties could be overcome. Combustion of fuel intimately mixed with air has the effect of communicating heat very rapidly to that part of the substance which is not involved in the chemical change, which is considerably the greater part of it, including all the nitrogen. This view of the matter correctly represents the main action which takes place in a gas or petrol engine. The change of state, including a change

Digitized by Google

of volume at given temperature and pressure, and a change of specific heat, of that smaller portion of the substance which undergoes chemical change, must not be left out of account. The effect produced is, in fact, approximately equivalent to a rapid communication of heat from an external source to the whole substance, assumed to be introduced into the cylinder at a temperature near that of the atmosphere, and with the chemical composition which it actually has after combustion. Calculations of the effect produced by the combustion are usually made (so far as the necessary data are available) on this assumption.

In connection with the evolution of heat in chemical changes, it is interesting to consider cases in which the chemical change is reversible and isothermal, heat being parted with during the change in one direction, and received during the change in the other direction; and to compare this with the analogous case of evaporation and condensation, see p. 22.

12. Continuous reversible processes. In order to trace the details of a continuous process in which a substance receives heat and does work, either as the working substance in a heat engine or under other conditions, the energy equation must be used in the form

$$dQ = dE + dW,$$

where dQ, dE and dW are corresponding elements of heat received, increase of energy, and work done, per unit mass of the substance, in an infinitesimal step of the process.

In the following theory of continuous processes it will be assumed in general: (1) that the kinetic energy of the substance is negligible, so that E represents its internal energy per unit mass; (2) that the processes which the substance undergoes are reversible; (3) that the state of the substance at any instant, in the course of the changes which it undergoes, may be specified by the values of not more than two quantities which may vary independently of one another.

The theory of processes under these conditions is the fundamental theory of the subject. With suitable modifications it may be applied to cases in which kinetic energy must be taken into account, or in which a process includes certain irreversible steps; these are matters to be considered individually as they arise. The third condition is of a somewhat different character from the other two. It is not adopted merely as a simplification, or because the case of a substance whose state

Digitized by Google

depends on two independent variables has important direct applications. As a matter of fact it is unnecessary to take a more general case, because it is found that, when the theory for two independent variables has been established, it can be extended so as to be applicable to cases in which more than two independent variables are required.

A reversible process is one which can be retraced, so that the substance passes through the same states as in the direct process, but in the reverse order; the amounts of heat received and of work done in each step being the same as in the direct process, but with opposite signs; heat being parted with where in the direct process it was received, and work being done upon the substance by some external agency where in the direct process it did work.

The direct transfer of heat which takes place between two bodies at different temperatures is an operation which cannot be retraced, so any portion of matter undergoing a reversible process must be all at one temperature. But merely receiving or parting with heat is a reversible operation, there being no stipulation in this case as to heat which is parted with in a reversed process being transferred to the same body as that from which it was received in the direct process. Thus it should be noted that two portions of matter, at different temperatures, may each undergo a reversible process, although the process for the two portions combined may be irreversible.

Reversible work must be due to elasticity of the substance*, and depends upon the substance being such that it has a definite state of stress when it is in all other respects in a given state, within the range of changes which it is supposed to undergo.

As an example of reversible work, consider that done by the spring of a spring balance, when gradually stretched or allowed to contract. Here the work done upon the spring, per unit length of it, during an elementary stretch, is equal to the product of the force exerted, and the increment of stretch; and both the force and the stretch are functions of whatever quantities specify the state of the spring at the instant in question. In more complicated cases of elastic strain of a solid substance the work can be expressed as a sum of such terms. The stretch must be produced or reduced slowly and gradually, the external force being that which balances the stress of the spring; otherwise the work done would be partly expended on setting up vibration of the spring, and would not be reversible.

* It is assumed that we are dealing only with mechanical work. Approximately reversible work may also be done electrically.

Digitized by Google

The most important case of reversible work is that which is done in balanced expansion, or compression, of an elastic fluid. We may practically confine our attention to this case, as being not only the most important one, but also typical of all others. A fluid has elasticity of volume only; the only stress is the pressure p, and dW is equal to pdv, where v is the volume per unit mass, or the "specific volume" of the fluid.

To prove this, suppose a mass m of the substance to expand in a cylinder, driving a piston of area A. The resultant force exerted on the piston by the fluid is Ap; and if this remains constant while the piston moves through a distance a, the work done is aAp. Now aA is the increase of volume, which may be denoted by $m\delta v$. Thus the work done, if the pressure remains constant, is $mp\delta v$. But the pressure generally varies during an expansion, so the work done must be regarded as the limit of the sum of infinitesimal amounts denoted by $mpdv$, or pdv per unit mass. The same expression applies to any case of balanced expansion; for the area of the surface of a fluid, bounded by any envelope, may be divided into elementary portions, on each of which we may imagine an elementary cylinder erected. If A_1, A_2..... are the areas of the several pistons, and a_1, a_2..... their displacements (positive or negative), the work done in an expansion is expressed by $(a_1A_1 + a_2A_2 + ...)p$, the limiting value of which is $mpdv$, or pdv per unit mass, as before.

A pair of quantities must be chosen as independent variables, in terms of which to specify the state of the substance. Sometimes p and v are a convenient pair of quantities for this purpose; but a variety of other choices may be made, each of which either has some theoretical advantage, or happens to suit some particular type of substance. In order to be able to refer to these quantities without committing ourselves to any particular choice, let us denote them by x and y. Any quantity, such as E, p, or v, or the temperature t, whose value depends on the state of the substance, and not on its past history, is a function of the independent variables, if it is not itself chosen as one of them.

The state of the substance at any instant may be represented by a point in a diagram in which x and y are rectangular coordinates; a process, in which the substance changes from a state 1 to a state 2, by continuous variations of x and y, is then represented by a line 12. A process may be such as to bring the substance back to its original state; it is then called a cyclical process, or a cycle, and is

Digitized by Google

represented by a closed line, the points 1 and 2 coinciding. It is convenient to mark points on the diagram representing states of the substance by numbers, which may be used as suffixes; thus E_1 and E_2 will be used to denote the values of the internal energy, per unit mass, of the substance in the states 1 and 2 respectively, which are represented by points marked 1 and 2. The range of possible values of x and y is sometimes limited by the definitions of these quantities; for example, density cannot be negative, and the proportion of water in wet steam must be between 0 and 1. In some cases a limit of the range of a variable corresponds to some crisis in the state of the substance, beyond which a new choice of variables may be needed.

An element dW of reversible work is either pdv or expressible in a form analogous to this; and thus, whatever choice is made of two independent variables, it may be written in the form

$$Rdx + Sdy,$$

where R and S are functions of x and y. It has a definite value for any elementary step dx, dy of a process, and the same value with opposite sign for the reversed step $-dx$, $-dy$. If reversed work has been secured for a retraced process, the heat received must also be reversed since $dQ = dE + dW$. Now E is a function of x and y, so

$$dE = \frac{dE}{dx}dx + \frac{dE}{dy}dy;$$

and if we write M for $\frac{dE}{dx} + R$, and N for $\frac{dE}{dy} + S$,

$$dQ = Mdx + Ndy,$$

where M and N are functions of x and y. On the assumption that R, S, M and N are known in terms of x and y for the substance in question, the amounts of work done and of heat received can be calculated for any given process. These amounts are generally different for different processes between two given states of the substance; but for a given process each has a perfectly definite value.

13. Adiabatic processes. A process in which no heat is received or parted with is called an adiabatic process, and when reversible is such that $Mdx + Ndy = 0$. This equation defines a system of lines on the diagram, which may be represented by an equation $f(x, y) = C$, where C is a constant for each line. The value adopted for C distinguishes one line from another. One of these

Digitized by Google

adiabatic lines may be drawn through any given point x_1, y_1 of the diagram, the value of C for this line being $f(x_1, y_1)$.

The existence of a quantity which is a function of x and y (that is to say of the state of the substance), and has the property of being constant for a reversible adiabatic process, so that its values may be used to distinguish one adiabatic line from another, is a fundamental feature of the theory. And the fact that this is derived from the first law of thermodynamics, in the case in which there are only two independent variables, accentuates the convenience of basing the theory on this case. The quantity possessing this property which is practically used, and the values of which are tabulated for steam and other important substances, is called the entropy of the substance. But this is a quantity the complete definition of which depends on the second law of thermodynamics. When there are three or more independent variables, the existence of a quantity whose value depends on the state of the substance, and which is constant in adiabatic processes, depends on the second law of thermodynamics.

14. Fluid working substance. For a fluid, at uniform pressure and temperature, the energy equation for reversible processes (the work unit being used) is

$$dQ = dE + pdv.$$

Suppose chemical changes to be excluded; then the state of the substance depends on two quantities which may vary independently. It is often convenient to take these two quantities to be p and v; a process is then denoted by a line drawn on a p, v diagram. An advantage of the use of this diagram is that in it work is represented by an area. The work done by the substance, per unit mass, during a process represented by a given line, is equal to $\int pdv$ along this line, and this integral is represented by an area in the way that has already been explained, p. 2. Thus this diagram exhibits to the eye the fact that the work done, and consequently also the quantity of heat received, in a process in which the substance undergoes a change from one given state to another, depends on the process and not merely on the initial and final states.

The temperature, t, is a function of p and v. The equation connecting these three quantities is called the "characteristic equation" of the substance. A process for which the temperature is constant is called an isothermal process. By means of the characteristic equation,

Digitized by Google

which must be determined by experiment for any given substance, a series of isothermal lines for various temperatures may be drawn on a p, v diagram.

If some other pair of independent variables, x and y, are chosen, p and v are functions of these, and dW may be written $p\frac{dv}{dx}dx + p\frac{dv}{dy}dy$. Take t as one of the independent variables, and denote the other one by y; then the energy equation may be written $dQ = M dt + N dy$. Here M is the "specific heat" of the substance when subject to the condition that y is constant. This condition specifies a certain process, which may be represented by a line in a diagram. For this process, defined by $dy = 0$, the energy equation is $dQ = M dt$.

The specific heat of a substance is the quantity of heat received by a unit mass of the substance per unit rise of temperature, while the substance is undergoing some reversible process. It is not a definite quantity for a given substance in a given state unless the process is sufficiently defined. In the case of solids and liquids, which are approximately incompressible, the substance is understood to be under ordinary laboratory conditions, and the effect of any variation in the conditions is insensible, thus the specification of a process is unnecessary. But for a gaseous substance specific heat has no meaning unless the process is explicitly defined. For any given state of the substance it has one value when the substance is being kept at constant volume, and another value when it is at constant pressure; it is zero for an adiabatic process, and a process may be such as to give a negative specific heat, a reduction of temperature as heat is received.

Digitized by Google

CHAPTER III

PARTICULAR TYPES OF SUBSTANCE

15. A vapour and its liquid. Consider the case of a substance consisting of a given vapour together with some of its own liquid, in equilibrium in a closed vessel, so that for any given temperature it has a definite pressure, namely the vapour pressure for that temperature. It does not matter whether the vapour and liquid are intimately mixed or not, provided that in either case the specific volume of the substance is reckoned as the ratio of the whole volume to the whole mass. An intimate mixture of vapour and liquid may be called wet vapour. The state of the substance depends on two independent quantities. One of these may be the temperature, and the other may be the dryness, that is to say the ratio of the mass of vapour to the whole mass. But several other choices may be made of a pair of independent variables, each of which possesses some feature which makes it convenient for certain purposes.

The vapour in equilibrium with its liquid is said to be saturated; and, so long as it is not condensed, its state depends on only one quantity, which may be the temperature. For any given vapour there is a certain "critical temperature," above which the mixture of liquid and vapour cannot exist, above which therefore the term saturated vapour has no application. For steam the critical temperature is about 365° C., for carbonic acid it is about 31° C., for hydrogen it is about −241° C. Below the critical point a given saturated vapour has a definite pressure, specific volume, energy and other characteristics for each temperature. These quantities may be tabulated for various temperatures, or their variations may be shewn by curves in a diagram; and any one of them may be used instead of the temperature as the independent variable.

The liquid portion of the substance has the same pressure as the vapour, as well as the same temperature, so its state is completely specified by the temperature. Variations in the volume of a liquid

Digitized by Google

are small, and in this connection are practically negligible. The energy of a liquid depends almost wholly on the temperature, so the energy of the liquid, in combination with vapour, is practically the same as that of liquid at the same temperature but at some different pressure.

Let the dryness of the substance be q; then we have a mass q of saturated vapour, and a mass $1-q$ of liquid, per unit mass of the substance. Thus the specific volume of the substance is $qV+(1-q)w$, where V and w are the specific volumes of the vapour and the liquid. The energy of unit mass of the substance is $qE_s+(1-q)E_w$, where E_s is the energy of the vapour, and E_w that of the liquid. Any other quantity depending on the dryness involves it in this simple way. Thus if we have tables of such quantities for the liquid alone and for the vapour alone, their values for the mixture can readily be calculated.

In the case of water and steam the energy is reckoned as zero for water at the freezing point, at the pressure of 760 mm. of mercury. The energy of water is practically equal to the quantity of heat received as its temperature is raised from this zero point, irrespective of changes of pressure; this will be denoted by h. As the specific heat of water does not differ much from unity, h in thermal units differs only slightly from the temperature reckoned from the ordinary zero.

Evaporation is reversible, the reverse operation being condensation. At constant volume the substance does no work, and the quantity of heat received during any change is equal to the increase of energy. But in practice the more important case of evaporation is that which takes place at constant pressure, as in the case of a steam boiler working steadily. In this case part of the heat received is accounted for by work done by expansion of the substance, as vapour is formed and has to make room for itself. The quantity of heat received during the evaporation of a unit mass of the liquid without change of temperature, and therefore also at constant pressure, is called the latent heat of the vapour. This terminology is derived from an obsolete theory of heat; but it is too well established to be changed now. The latent heat is denoted by L, and for a given vapour has a definite value for each temperature, and may be tabulated. The usual practice is to reckon such quantities as L and E in terms of a thermal unit, thus

$$L = E_s - E_w + Ap(V-w),$$

where A stands for $1/J$.

Digitized by Google

If a steam boiler is working steadily, receiving feed water at the temperature t_0, and producing steam of dryness q_1 at temperature t_1, the quantity of heat which it receives per unit mass of feed supplied, or steam produced, is $h_1 - h_0 + q_1 L_1$.

16. Superheated vapour. The temperature of vapour not in contact with liquid may be raised above that of saturated vapour at the same pressure. The vapour is then said to be superheated, and its state depends on two quantities, which may be the temperature and the pressure. A supply of superheated vapour, such as steam, is generally produced at constant pressure; thus the specific heat of the superheated vapour at constant pressure is an important quantity to be determined experimentally. Denote this by k, then k is a function of t and p, and $\int_{t_1}^{t_2} k dt$ represents the quantity of heat required for raising the temperature of the vapour from t_1 to t_2 at constant pressure. The variation of k is not rapid, and if its average value for a given process is estimated to be k', the quantity of heat required is $k'(t_2 - t_1)$. For steam the value of k, within ordinary ranges of temperature and pressure, varies between about 0·48 and 0·59, decreasing with rise of temperature, and increasing with rise of pressure.

17. E + Apv. The quantity $E + Apv$, for a fluid, is found to be useful for various purposes, its use not being confined to the case of a vapour and its liquid. It will be denoted by the symbol I. It would be convenient to give it a name, but unfortunately no name has been found for it sufficiently appropriate to have met with general acceptance. It is sometimes called the "total heat" of the substance to which it refers; and various other names have been suggested, such as "total energy," which is also unsatisfactory. It is a function of the state of the substance, with a definite value for a given fluid in a given state; and is not related to any particular process. Its value for wet vapour, of dryness q, is clearly equal to $qI_s + (1-q)I_w$, where the suffixes s and w refer respectively to saturated vapour and to liquid at the same temperature and pressure.

For any reversible process

$$dI = dE + Apdv + Avdp = dQ + Avdp.$$

Thus for a constant pressure process from a state 1 to a state 2, the quantity of heat received by the substance is $I_2 - I_1$. For

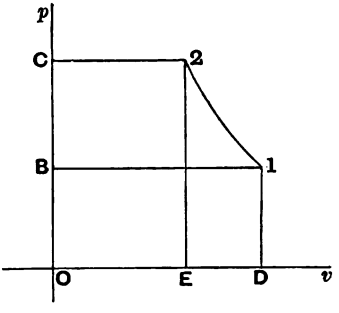
Digitized by Google

example $L = I_s - I_w$, and tables of I may, if we like, supersede the use of L*.

For an adiabatic process from a state 1 to a state 2

$$I_2 - I_1 = A\int v\,dp \text{ along an adiabatic line from 1 to 2.}$$

Now $\int v\,dp$ is equal to the area $12CB$ in a p, v diagram, and this is equal to the work done in adiabatic compression of the substance from a pressure p_1 to a pressure p_2, together with the work done in forcing it into a receiver at pressure p_2, assuming the lower pressure p_1 to be behind the piston during this process; for the work done in compression is $12ED$, the work done in forcing the substance into the receiver at constant pressure is $2COE$, and from the sum of these must be subtracted the work done by the pressure behind the piston, namely $1BOD$.



Let us find, in terms of I, the quantity of heat required to produce steam, whether wet or dry or superheated; the evaporation and the superheating, if any, taking place at one constant pressure. It will be assumed that variations of the specific volume, w, of water are negligible, so that any amount of heat which it receives is equal to the increase of its internal energy; also that its specific heat is independent of its pressure, so that the internal energy is a function of the temperature only. Start with feed water supplied to the boiler in a state denoted by 0. Let 1 denote the state of water at the temperature and pressure of the boiler. Let 2 denote the state of the substance as finally produced in the form of steam, wet or dry or superheated. The quantity of heat received, per unit mass, during the change from 0 to 1 is equal to $E_1 - E_0$, that is to say

$$I_1 - I_0 - Aw\,(p_1 - p_0).$$

The change from 1 to 2 is at constant pressure, so the quantity of heat

* Willard Gibbs wrote, with reference to this property of I, "This function may therefore be called the *heat function for constant pressure* (just as the energy might be called the heat function for constant volume)."

Digitized by Google

received during this change is $I_2 - I_1$. Thus the total quantity of heat required per unit mass of the substance for the change from 0 to 2 is

$$I_2 - I_0 - Aw(p_2 - p_0),$$

since $p_1 = p_2$. Here I_0 is I_{w0} (which means I_w for the temperature t_0) provided that p_0 is the pressure of saturated steam for the temperature t_0. If this is not the case let us write p' for this pressure, then the expression for the quantity of heat required may be written

$$I_2 - I_{w0} - Aw(p_2 - p').$$

The terms $Aw(p_2 - p_0)$ and $Aw(p_2 - p')$ are so small as to be almost insignificant. If the thermal unit is that which is based on whatever unit mass we are using and the centigrade degree, their value is about 0·17 for every 100 pounds per square inch of pressure difference. $Aw(p_2 - p_0)$ is the thermal value of the work required to pump a unit mass of feed water into the boiler.

If the steam which is produced is superheated

$$I_2 = I_{s1} + \int_{t_1}^{t_2} k dt,$$

where I_{s1} is the value of I for dry saturated steam at the same pressure. Or if k' is taken as the average value of the specific heat of superheated steam at constant pressure for the process in question

$$I_2 = I_{s1} + k'(t_2 - t_1).$$

18. Throttled vapour. Suppose that steam, wet or dry, or any other elastic fluid, is being converted from a state 1 to a state 2 by passing steadily through a restricted aperture, without receiving or parting with heat, the pressure being thus reduced by an irreversible process, which cannot be represented on a diagram. At the aperture there is turbulent motion, which gradually subsides; and it will be assumed that in the states 1 and 2 the kinetic energy is negligible. Consider a certain quantity of the fluid, chosen so as to include all the fluid which is in the neighbourhood of the aperture, and some fluid on one side of this in state 1, and some on the other side of it in state 2. During the passage of a unit mass of the fluid through the aperture, the whole quantity of fluid under consideration acquires an amount of energy which in thermal units is $A(p_1 v_1 - p_2 v_2)$, this being the net amount of work done upon it. But in steady working the only change which this quantity of fluid experiences is that the amount in state 1 is reduced by a unit mass, and the amount in

Digitized by Google

state 2 is increased by a unit mass. Thus $E_2 - E_1 = A(p_1v_1 - p_2v_2)$, that is to say $I_2 = I_1$.

For wet vapour, if p_1 and p_2 and the initial dryness, q_1, are known, this equation, which takes the form

$$q_2 I_{s2} + (1 - q_2) I_{w2} = q_1 I_{s1} + (1 - q_1) I_{w1},$$

gives q_2 by means of tables of I_s and I_w. This equation may however give a value of q_2 which is impossible on account of being greater than unity; this indicates that the substance in state 2 is superheated. In this case, on the assumption that a constant quantity, k, may be taken as the specific heat of the superheated vapour at constant pressure, the equation takes the form

$$I_s + k(t_2 - t) = q_1 I_{s1} + (1 - q_1) I_{w1},$$

where t and I_s refer to saturated vapour at the pressure p_2. This gives the temperature t_2 of the superheated vapour, subject to any error that may be due to a faulty estimate of an average value for the specific heat.

The same calculation applies if the pressure is reduced by friction in a pipe, without any energy being lost by conduction of heat through the material of the pipe. Also if there is loss of energy by conduction of heat through the material of the pipe, the amount of this loss per unit mass of the substance traversing the pipe is $I_1 - I_2$, and may be calculated if the pressure and dryness at both ends of the pipe are known.

Similar calculations may be made if the kinetic energy of the substance is not negligible. Denote its velocity in the states 1 and 2 by u_1 and u_2, then the energy per unit mass in state 1 is $E_1 + \frac{A}{2g} u_1^2$, and the energy in state 2 is $E_2 + \frac{A}{2g} u_2^2$, and if no heat is received or parted with, $\frac{A}{2g}(u_1^2 - u_2^2)$ is equal to $I_2 - I_1$. If the areas of sections of the pipe at inlet and outlet are a_1 and a_2, $\frac{a_1 u_1}{v_1}$ and $\frac{a_2 u_2}{v_2}$ are each of them equal to the mass of the substance passing through per unit time*.

The property of I, that it is unchanged by a throttling of the

* It is assumed that A refers to a gravitational unit of work; that is to say, if a foot and a pound are the units of length and mass, it is the number of thermal units in a foot-pound.

Digitized by Google

substance, or its passage through a porous plug, is not especially related to this particular process. It is clear that if a fluid experiences any change in which it does not receive or part with energy, except that due to the work done by pressure behind it and in front of it, I remains unchanged, assuming that the kinetic energy is negligible before and afterwards. For example this is the case for a chemical change of the substance.

19. Perfect gas. The most permanent gases conform approximately to the following empirical laws, namely: (1) the characteristic equation has the form $pv = Rt$, where R is a constant with a special value for each gas, and t is the temperature measured from the absolute zero; (2) the internal energy, E, is a function of the temperature only; (3) the specific heat at constant pressure is constant for a given gas. These properties, which no actual substance possesses with perfect accuracy, are called the properties of a perfect gas. The term perfect gas provides a concise way of referring to them, analogous to the use of the term rigid body in dynamics.

It will be found that the properties of a perfect gas are consistent with the second law of thermodynamics, which in fact requires that a substance which satisfies the first condition should obey the second also.

The deviations of the properties of any of the more permanent gases from those which define a perfect gas are, throughout a considerable range of temperature and pressure, small enough to be generally negligible. But their existence is well recognised, and for some purposes they are of great importance; just as the small yield of an approximately rigid body is for some purposes of fundamental importance. In the liquefaction of gases important use is made of the dependence of internal energy on specific volume; and for some gases the specific heat at constant pressure increases to an important extent at high temperatures.

For a perfect gas, E being a function of t only, dE may be written in the form $k\,dt$. Thus for a reversible process, work being done by balanced expansion, $dQ = k\,dt + A\,p\,dv$, heat and energy being measured in thermal units in accordance with the usage of heat tables. For a constant volume process this equation is $dQ = k\,dt$, thus k is the specific heat at constant volume. The characteristic equation gives $p\,dv + v\,dp = R\,dt$, thus we get

$$dQ = (k + AR)\,dt - v\,dp;$$

Digitized by Google

accordingly $k + AR$ is the specific heat at constant pressure. This by hypothesis is a constant for each gas, so k is also a constant. Let us write k_v for k, and k_p for $k + AR$.

When heat is applied to raise the temperature of the gas at constant volume, the whole of it is expended on increasing the internal energy; but when the gas is kept at constant pressure, the same rise of temperature involves the same increase of internal energy as before, and the work which the gas does as it expands has also to be provided for. This accounts for the result obtained above, namely, $k_p - k_v = AR$.

Thus we have obtained two equivalent forms for the energy equation for a perfect gas, namely:

$$dQ = k_v dt + Ap dv \quad \text{.....(1),}$$

$$dQ = k_p dt - Av dp \quad \text{.....(2).}$$

The first of these is appropriate to the case in which t and v are used as independent variables, and the second to the case in which t and p are so used. A third form may be found which is appropriate to the case in which v and p are used as independent variables, namely

$$\frac{dQ}{t} = k_v \left(\frac{dp}{t} + \frac{dv}{v}\right) + AR \frac{dv}{v},$$

since the characteristic equation gives $\frac{dt}{t} = \frac{dp}{p} + \frac{dv}{v}$. The symbol γ is used for the ratio $\frac{k_p}{k_v}$, so that $\frac{AR}{k_v} = \gamma - 1$; thus the energy equation may be written

$$\frac{dQ}{t} = k_v \left(\frac{dp}{p} + \gamma \frac{dv}{v}\right) \quad \text{.....(3).}$$

This equation shews that $\frac{dQ}{t}$ is a perfect differential of a function of the variables which specify the state of the substance, being in fact equal to $d\{k_v \log (pv^\gamma)\}$. It will be found, from the second law of thermodynamics, that the fact that $\frac{dQ}{t}$ is a perfect differential, which is implied in the properties assumed for a perfect gas, is a general property possessed by all substances undergoing reversible processes. The quantity denoted by γ is an important one, on account of the fact that it has nearly the same value, about 1·4, for all the more permanent gases.

For any given temperature and pressure, the ratio of either k_v or k_p

Digitized by Google

to the specific volume has nearly the same value for all approximately perfect gases. In fact the characteristic equation may be written $\frac{k_v}{v} = \frac{A}{\gamma - 1}\frac{p}{t}$. Thus instead of using the ordinary specific heats which are referred to unit mass of a gas, it is sometimes convenient to use what has been called the "volumetric heat." This is the quantity of heat received at constant volume, per unit rise of temperature, by a quantity of the gas which, at a standard temperature and pressure, occupies a unit volume, or some other standard volume. Thus the volumetric heat has nearly the same value for all approximately perfect gases.

The theory for a perfect gas is peculiarly simple. For a given gas two constants are to be determined experimentally. But as γ has nearly the same value for different gases, calculations for a given gas mainly depend on one quantity peculiar to the gas, namely R. The quantity of heat received in a given process may be calculated, if the process is defined by an equation connecting the variables. The value of the specific heat for any process is $k_v + Ap\frac{dv}{dt}$; the differential coefficient, $\frac{dv}{dt}$, being found from the equation which defines the process. Conversely, if the rate at which the substance is receiving heat is given, we have a differential equation which defines the process. The total quantity of heat received during a reversible change of the substance from one given state to another is to be found by integration, and depends not only on the initial and final states, but also on the route by which the change takes place.

An isothermal process at temperature t is given by $pv = Rt$, thus isothermal lines on a p, v diagram are rectangular hyperbolas. The slope of such a line is equal to $-\frac{p}{v}$. The quantity of heat received in an isothermal process is equal to the amount of work done, the internal energy remaining constant.

An adiabatic process is given by $dQ = 0$, or $\frac{dp}{p} + \gamma\frac{dv}{v} = 0$, which gives, by integration, $pv^\gamma = \text{constant}$. Thus adiabatic lines on a p, v diagram are similar in character to hyperbolas, but have a steeper slope, namely $-\gamma\frac{p}{v}$. They are not symmetrical with regard to the axes, but approach the axis of v more rapidly than the axis of p.

The work done by the substance during a reversible change from a

Digitized by Google

state 1 to a state 2 is equal to $\int p dv$ for the process from 1 to 2. For an isothermal process at temperature t this is $Rt \int_{v_1}^{v_2} \frac{dv}{v}$, that is to say $Rt \log \frac{v_2}{v_1}$. For an adiabatic process from 1 to 2 the work done is equal to the loss of internal energy, namely, in thermal units, $k_v (t_1 - t_2)$. This may also be found from $\int p dv$ along an adiabatic line, given by $pv^\gamma = C$; thus it is $C \int_{v_1}^{v_2} v^{-\gamma} dv$, which may be written $\frac{p_1 v_1 - p_2 v_2}{\gamma - 1}$. This is equal to $\frac{R(t_1 - t_2)}{\gamma - 1}$. In the same way the amount of work done may be calculated, by integration, for any other given path on a p, v diagram. For example, if the gas passes from the state 1 to the state 2 by a constant pressure process followed by a constant volume process, the work done is $p_1 (v_2 - v_1)$.

If the work unit of energy were used throughout, the symbol A would be omitted from these equations. It is often convenient to use this unit in order to get rid of A. The thermal unit is however generally used in practical calculations, and specific heats are quoted in terms of this unit. If we adopt the thermal unit which is based on the pound as unit mass and the centigrade unit of temperature, also a pound per square foot as unit of pressure, with a cubic foot as unit of volume; then the work unit of energy is a foot-pound, and J or $1/A$ is about 1400. A point of convenience in the use of the thermal unit for heat tables is that all quantities in thermal units, per unit mass of a substance, are independent of the choice of a unit of mass. Specific heats in thermal units are independent of the choice of unit of temperature.

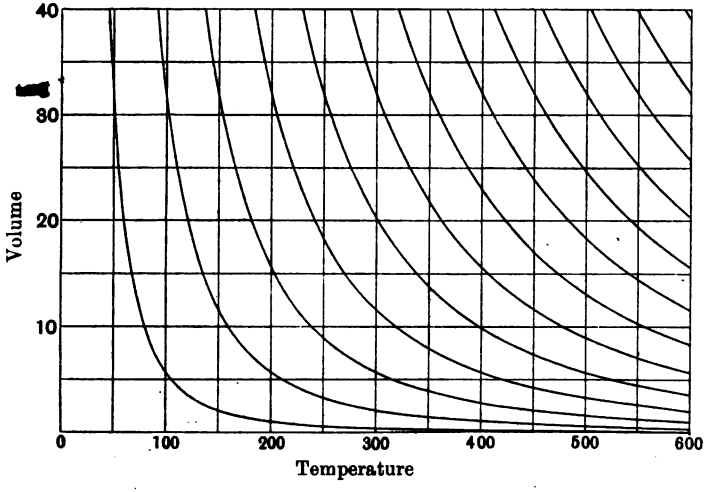
For the purpose of the theory of air engines, or air compressing, air may be treated as an accurately perfect gas. But with the high temperatures reached in the cylinders of internal combustion engines, divergences of the behaviour of gases from that of the ideal perfect gas become more important, and have not been fully traced. A gas receives heat from surrounding bodies, such as the walls of a cylinder, or parts with heat to them, rather slowly in comparison with the rate at which machinery is worked; so when air is compressed by a piston in a cylinder, or expands in the cylinder of an air engine, the process approximates to being adiabatic*.

* In this connection the most important property of air and other gases is that

Digitized by Google

For an adiabatic process $pv^\gamma = \text{constant}$; that is to say (since pv is equal to Rt), $tv^{\gamma-1} = \text{constant}$, and $tp^{\frac{-\gamma-1}{\gamma}} = \text{constant}$. These three equations represent the adiabatic lines, for a perfect gas, on a p, v diagram, a v, t diagram and a p, t diagram respectively.

The adiabatic lines, $tv^{\gamma-1} = C$, on a v, t diagram, are of the same character as the adiabatic lines on a p, v diagram. Their slope to the axis of t is $-\frac{1}{\gamma-1}\frac{v}{t}$. They all have the same shape and differ only in scale, according to the value given to C. Thus to draw them it is only necessary to find points on one line by calculation; the other



Curves $tv^{0\cdot4} = C$, *for* $C = 200, 400, 600, \ldots\ldots$

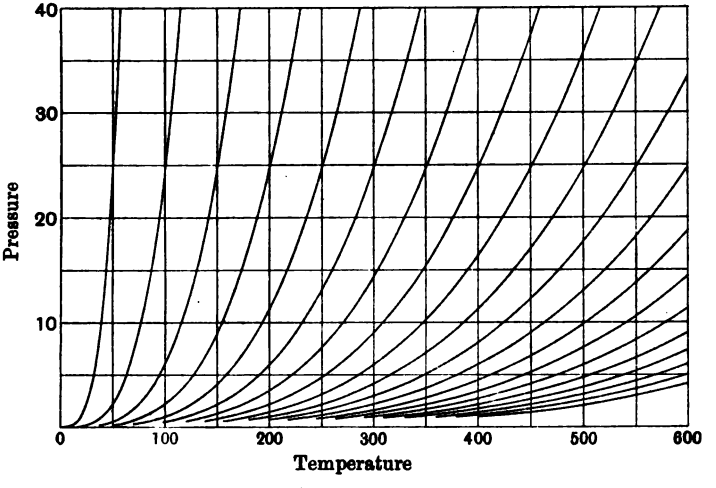
lines can be derived from this one by variation of the scale. In the diagram given here the lines are accurately drawn for $\gamma = 1{\cdot}4$, for equal intervals of temperature for any given volume; so that the change of temperature for any given adiabatic expansion, or compression, may be found by following one of the lines, assuming the

they are very bad conductors of heat. Thus it has been found by experiments on the rapid compression and expansion of air in a cylinder, without internal combustion, that an important factor in the conditions which produce deviation of the indicator diagram from that of an adiabatic process, is the extent to which currents are set up by rapid rush of the air through valves. Such currents disturb the protection which would be afforded to the main body of air in a cylinder, by a thin layer immediately in contact with the cylinder walls, if the air were comparatively quiescent.

Digitized by Google

value taken for γ to be correct. Any units of volume and temperature may be used. If a temperature beyond 600° absolute occurs, two degrees may be taken as the unit, giving a range of 1200°.

The adiabatic lines, $t = Cp^{\frac{\gamma-1}{\gamma}}$, on a p, t diagram, all touch the axis of t at the origin. Their slope to the axis of t is $\frac{\gamma}{\gamma-1}\frac{p}{t}$. They differ from one another only in scale. The lines in the diagram given



Curves $t = Cp^{\frac{2}{7}}$, *for* $C = 20, 40, 60, \ldots\ldots$

here are accurately drawn for $\gamma = 1{\cdot}4$, and for equal intervals of temperature for any given pressure. For a gas with this value for γ, the change of temperature in adiabatic expansion or compression, from one given pressure to another, may be traced by following one of the lines of the diagram; any units of pressure and temperature being taken.

A simple way of obtaining numerical results graphically, though it does not exhibit them so clearly to the eye, is to plot the logarithms of p, v and t. The isothermal, adiabatic, constant pressure, and constant volume lines on the diagrams for a perfect gas, with these logarithms for coordinates, are then straight lines. Entropy may be included among the quantities studied by straight line diagrams, but its value is to be plotted simply, not its logarithm.

Digitized by Google

CHAPTER IV

THE SECOND LAW OF THERMODYNAMICS

20. The second law of thermodynamics is the central feature of the theory of heat, the thing which is characteristic of it, distinguishing it from other branches of the theory of energy. The theory which it formulates deals with the question of the availability of heat received by a system for the production of mechanical work. This question is the most conspicuous one which is raised by the practical applications of heat by engineers. Why, for example, is a marine steam engine permitted to waste the greater part of the energy received by the boiler as heat, in slightly raising the temperature of the sea? What are the conditions which limit its efficiency in producing work? Is it possible that a more efficient result could be obtained merely by employing some other working substance in the place of steam? The characteristics of heat have been partly expressed already by the recognition of temperature as a measurable property of every portion of matter. The second law of thermodynamics may be regarded as an extension of the theory of temperature. It gives, in terms of temperature, certain general results which apply to all working substances.

The fact expressed by this law may be stated in a variety of different ways. The form of statement adopted by Clausius is the one which most directly connects the law with the elementary theory of temperature. This statement is that it is not possible for a self-acting machine, unaided by external agency, to transfer heat from a body at a lower to a body at a higher temperature.

It should be noted that an apparatus is not to be regarded as a self-acting machine if it works at the expense of some permanent change in the apparatus itself. In order that it may be a self-acting machine, in the sense in which the term is used here, any change which it undergoes in the course of its operations must be such that it can resume its initial state without external aid, and thus perform

Digitized by Google

cycles, repeating its operations any number of times. Accordingly the second law of thermodynamics is a statement about cycles.

In a statement which takes account of a complete cycle of changes of a system, at the end of which it returns to its original state, the special characteristics of the system are naturally to some extent eliminated. If a body which is receiving heat and doing work performs a cycle, the net amount of heat received in the process is equal to the net amount of work done. The body acts as a vehicle of energy, its own energy being on the whole unchanged.

21. Example of apparatus for transferring heat. The way in which heat may be transferred from a body at a lower to a body at a higher temperature, by the intervention of suitable apparatus, will be understood from the following example. Suppose that we have two bodies, A and B, each maintained at a constant temperature, that of A being higher than that of B. To transfer heat from B to A let us employ some compressed air, and the appliances necessary for compressing it adiabatically, or allowing it to expand adiabatically doing work, or for placing it in contact with either A or B. Let this air expand till it is cooler than B, and then at constant volume take some heat from B; let it then be compressed till it is hotter than A, and then at constant volume part with the same quantity of heat to A. According to the second law of thermodynamics, whether the substance employed is air or any other substance, such an operation as this cannot be self-acting.

Let us suppose that the operation is conducted so that, on the whole, no work has to be supplied from an external source, the work done by the air in expansion being equal to that employed for the subsequent compression. The air has then the same energy after the operation as it had before. This is possible; but our law states that the air cannot have performed a cycle, it must have undergone changes which it cannot recover from without external aid.

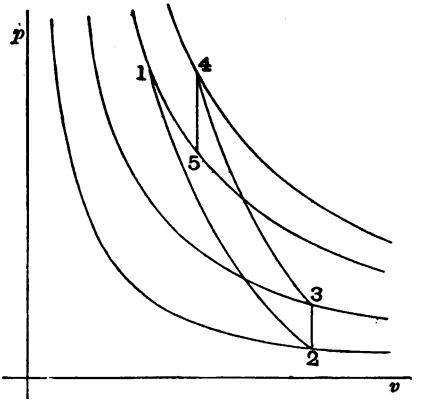
Calculations can be made for the case of air if we assume that it behaves as a perfect gas. Let the expansion be from a temperature t_1 to a temperature t_2, and the compression from t_3 to t_4. Draw on a p, v diagram the isothermal lines for these four temperatures; and represent the changes which the substance undergoes by a line 12345; 12 and 34 being adiabatic lines (drawn in the figure with exaggerated slope). As there is no change of energy $t_5 = t_1$; and as the quantity of heat taken from B is equal to that parted with

Digitized by Google

to A, $t_3 - t_2$ is equal to $t_4 - t_5$. Thus if values are chosen for t_1, t_2, t_3 and v_1, the whole process is determined. The temperature t_1 is to be not less than that of A, and the temperature t_3 not greater than that of B. It is easy to calculate the ratio of v_5 to v_1, and to shew that this is greater than unity. Denote $t_3 - t_2$, or $t_4 - t_1$, by a positive quantity λ. The equations of the two adiabatic steps of the process give $t_1 v_1^{\gamma-1} = t_2 v_2^{\gamma-1}$ and $t_3 v_3^{\gamma-1} = t_4 v_4^{\gamma-1}$, and the result is

$$\left(\frac{v_1}{v_5}\right)^{\gamma-1} = 1 - \lambda\left(\frac{1}{t_3} - \frac{1}{t_1}\right) - \frac{\lambda^2}{t_1 t_3};$$

now the right-hand side of this equation is clearly less than unity. A similar operation, 5 6 7 8 9, may be performed, starting from 5 and using the same four isothermal lines, the point 9 being on the



isothermal 1 5, and the volume being again increased. Each operation is performed without any expenditure of energy, but at the cost of an increase of the volume and decrease of the pressure of the gas. The apparatus is not self-acting.

In the case of an ordinary refrigerating machine the working substance is required to perform a cycle, so that the operation may be repeated. External aid is provided in the form of power supplied to drive the machine; and the quantity of heat which the working substance parts with at the higher temperatures is greater than that which it receives at the lower temperatures.

22. Carnot's engine. It is clear that a negative form of statement of the second law of thermodynamics is not convenient for practical use for the purpose of calculations, and that it is important

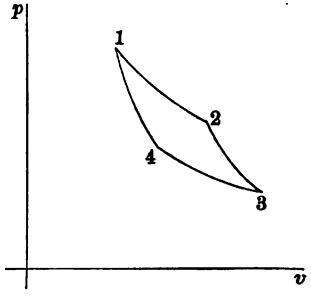
Digitized by Google

that the law should, if possible, be put into the form of a positive statement. This can be done by means of the theory of the Carnot engine.

Take as before two bodies, A and B, each maintained at a constant temperature, that of A being greater than that of B; also a given quantity of some elastic substance, at uniform temperature, which is capable of reversible expansion, and whose state may be specified by the values of two quantities. To simplify the description of the process which the substance is to undergo, let us suppose that it is a fluid whose state is specified by its pressure and specific volume; and that it has the usual property of having its temperature raised when it is compressed adiabatically, and lowered when it does work by adiabatic expansion. The description can be adapted to suit the case of a substance with the property of being cooled by compression, or one which does work of some type other than pdv.

In a reversible adiabatic process $\frac{dp}{dv}$ must be negative. It can be shewn that the existence of a substance for which $\frac{dp}{dv}$ is positive in adiabatic processes would violate the law of conservation of energy.

Start with the substance at the temperature of A; and let it expand doing work, but placed in such intimate contact with A that the tendency of the temperature to fall is constantly checked by a passage of heat from A. Thus, if the operation is sufficiently slow, we get an isothermal expansion, represented in a p, v diagram by the line 12, the substance receiving a certain quantity of heat from A at the temperature of A. Let the contact of the substance with A be now broken, and let it expand adiabatically till, in the state 3, its temperature is reduced to that of B. Let the substance be now slowly compressed in contact with B, the tendency of the temperature to rise being constantly checked by a passage of heat to B; thus we get an isothermal compression 34 at the temperature of B. Next let the contact with B be broken, and let the substance be compressed adiabatically till its temperature is raised to that of A. Let the range of the third operation, isothermal compression, be so chosen that the point 4 lies on an adiabatic line through 1; the fourth



Digitized by Google

operation then restores the substance to the state 1. Thus the substance performs a cycle. Its energy is restored at the end of the process to its initial value, consequently the net quantity of heat which it has received is equal to the net amount of work which it has done. Let Q be the quantity of heat received from A, and Q' the quantity of heat parted with to B, then the net amount of work done is equal to $Q - Q'$; and the efficiency of the arrangement, regarded as an engine whose function is to produce work from heat supplied by A, is $\frac{Q - Q'}{Q}$.

An apparatus arranged for performing these operations, in combination with a given source and sink of heat (A and B), is called a Carnot engine. It has the important feature of being a reversible engine. This means that the operations which have been described can be retraced, the working substance performing the cycle 14321. It means not merely that the process 12341 is a reversible one, but also that the transfers of heat between the working substance and the bodies A and B are reversible. It is clear in fact that, as transfers of heat take place only when the substance is at the temperatures of A and B, the reverse operation is possible in the same sense as the direct one is, that is to say under ideal conditions, all movements being sufficiently slow, and absence of friction being assumed. In the reverse operation, the substance is allowed to expand adiabatically, doing work, along the line 14; then expands isothermally in contact with B, taking in the quantity Q' of heat; then is compressed adiabatically along the line 32; and finally is compressed isothermally in contact with A, parting with the quantity Q of heat. This operation requires the application of external work to drive the engine, the net amount so applied being $Q - Q'$.

Any apparatus whose function is to produce work may be called an engine. But let us restrict the application of this term, for the present, to an apparatus employing a working substance which performs a cycle, receiving heat only from a source at a given temperature, and parting with heat only to a sink at a given lower temperature. Such an engine is said to work between these two temperatures. Using the term engine in this sense, it can be proved that all reversible engines working between two given temperatures have the same efficiency, though they may employ different working substances, or differ in other respects; also that no engine working between two given temperatures can have a greater efficiency than a reversible engine working between these temperatures.

Digitized by Google

To prove this, let us suppose that we have a reversible engine which, in each cycle, takes heat Q from a source A, and parts with heat Q' to a sink B, doing work $Q - Q'$ with efficiency $\frac{Q-Q'}{Q}$; also an engine not required to be reversible, which in each cycle takes heat H, at any temperatures, from the same source, and parts with heat H', at any temperatures, to the same sink, doing work $H - H'$ with efficiency $\frac{H-H'}{H}$. Let the second engine be of such size that $H - H' = Q - Q'$, so that it may be employed to drive the first engine reversed, while the working substance of each performs a cycle. The two engines thus combined form a self-acting machine. Suppose, if possible, that the efficiency of the second engine is greater than that of the first, so that H is less than Q, and consequently H' less than Q'. Then this self-acting machine transfers a positive quantity $Q - H$ of heat from B to A in each cycle. This being forbidden by our law, H cannot be less than Q; the efficiency of the second engine cannot be greater than that of the first; and if both engines are reversible, so that either can be used to drive the other, their efficiencies must be equal. The Carnot engine is a reversible one, therefore all Carnot engines working between two given temperatures have the same efficiency; the value of the ratio Q/Q', which determines the efficiency, is the same for them all, and depends only on the two temperatures.

In the case of a steam engine with surface condenser the working substance performs a cycle. Suppose that the steam is not superheated before it is used, then the highest temperature attained by it is that of the boiler, and the lowest temperature is that of the condenser. If the two extreme temperatures are given, there is a definite limiting value which the efficiency of the engine cannot exceed, this being the efficiency of a reversible engine working between these temperatures; and this limit is the same whatever working substance is used. To find the value of this quantity in terms of the temperatures it is only necessary to study the properties of some one substance.

23. Carnot cycle. The result which has been obtained, as to the efficiency of a Carnot engine, may be stated without any mention of an engine; for it has reference only to the cycle which is performed by the working substance. This cycle 12341, consisting of alternate isothermal and adiabatic reversible processes, is called a Carnot cycle. Take any number of Carnot cycles for different substances, or employing

Digitized by Google

different adiabatics, but agreeing in having the same temperatures, t and t', for the two isothermals 12 and 43. Then the ratio of the quantity of heat Q, received during the isothermal process 12, to the quantity Q', received during the isothermal process 43, is the same for them all, and depends only on the two temperatures. For any given pair of temperatures this ratio has a definite numerical value, which is the same for all substances and for all pairs of adiabatics. This is the second law of thermodynamics, for reversible processes, in the form of a positive statement.

24. Thermodynamic scale of temperature. To find the value of the ratio Q/Q' for various pairs of temperatures, it is only necessary to find it for some one substance, and some one pair of adiabatic lines. If we could assume the existence of a perfect gas, we could find it in terms of the temperatures measured by a perfect gas constant volume, or constant pressure, thermometer, as follows. The perfect gas laws give $Q = Rt \log \frac{v_2}{v_1}$, and $Q' = Rt' \log \frac{v_3}{v_4}$; also

$$v_2^{\gamma-1} t = v_3^{\gamma-1} t' \quad \text{and} \quad v_1^{\gamma-1} t = v_4^{\gamma-1} t',$$

so that $\frac{v_2}{v_1} = \frac{v_3}{v_4}$, that is to say $\frac{Q}{Q'} = \frac{t}{t'}$.

No actual gas exists which obeys these laws accurately; but we can infer from this calculation that Q/Q' for any substance is, for a wide range of temperature, very nearly equal to t/t', when temperature is measured by the hydrogen thermometer from the absolute zero of that thermometer. Accordingly by a slight adjustment of the hydrogen thermometer scale, we can obtain a scale of temperature for which the equation $Q/Q' = t/t'$ is accurately true. This is the thermodynamic or absolute scale.

The definition of this scale, with a centigrade unit, may be stated as follows. Let Q be the quantity of heat received by some given substance, in a reversible isothermal process, between two given adiabatic lines; then the magnitude of the temperature is defined as being λQ, where λ is a number which is chosen so that the difference of the temperatures of boiling water and melting ice, at a pressure of 760 mm. of mercury, is 100.

Using this scale we have $Q/Q' = t/t'$ as the statement of the second law of thermodynamics, and $\frac{t-t'}{t}$ as the value of the efficiency of a reversible engine working between the temperatures t and t'.

Digitized by Google

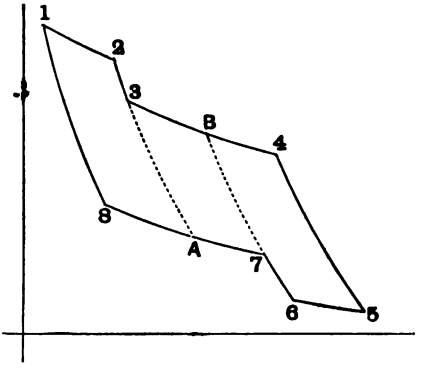
The thermodynamic scale of temperature is based on a general property of matter, and not on the special properties of any particular substance. It would be possible to use a different scale, preserving this characteristic; but in that case the mathematical expression of the second law of thermodynamics would assume a different form. The advantages of the particular scale which is chosen are its close agreement with the gas thermometer scales, and the simplicity of form of the equation $Q/Q' = t/t'$.

25. Any reversible process. The equation thus established for a Carnot cycle can be put into a form which is applicable to any reversible process. Let the quantity of heat received during a given process be divided into portions Q_1, Q_2, ... according to the temperature of the substance, the algebraical quantity Q_1 being received when the temperature of the substance is t_1, Q_2 when its temperature is t_2, and so on; and let us write $\Sigma \frac{Q}{t}$ to denote the sum $\frac{Q_1}{t_1} + \frac{Q_2}{t_2} + \ldots\ldots$. If heat is being received during a change of the temperature, $\Sigma \frac{Q}{t}$ assumes the form $\int \frac{dQ}{t}$, where dQ represents the quantity of heat received at temperature t. This integral represents the sum in question in any case, but the expression $\Sigma \frac{Q}{t}$ suffices in cases in which heat is received only during isothermal steps of the process.

With this notation the property of a Carnot cycle is written $\Sigma \frac{Q}{t} = 0$; and from this it can be proved that $\Sigma \frac{Q}{t}$, or $\int \frac{dQ}{t}$, is zero for any reversible cycle. Suppose the state of the substance to be specified by two quantities x and y, so that a reversible process is represented by a line in a diagram in which x and y are coordinates; and take, in the first place, a cycle in which heat is received only during isothermal steps. Then the area bounded by the cycle can be divided by adiabatic lines into areas such that the boundary of each is a Carnot cycle. For example if the cycle is 12345678 1, as shewn in the figure, 12, 34, 56, and 78 being isothermal steps, and 23, 45, 67 and 81 adiabatics, the dotted adiabatic lines $3A$ and $7B$ divide the area in this way. Let us denote the quantity of heat received in the process 12 by Q_{12}, and the temperature of the substance during this process by t_{12}, and so

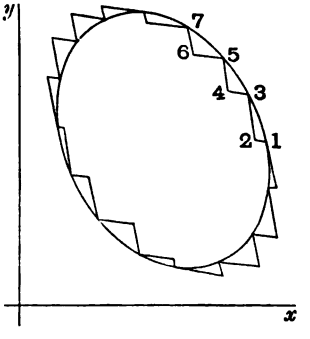
Digitized by Google

on. In this example, since 12A8 is a Carnot cycle $\frac{Q_{12}}{t_{12}} + \frac{Q_{A8}}{t_{A8}}$ is zero;



similarly $\frac{Q_{3B}}{t_{3B}} + \frac{Q_{7A}}{t_{7A}}$ and $\frac{Q_{B4}}{t_{B4}} + \frac{Q_{56}}{t_{56}}$ are each zero. Now the sum of these expressions makes up $\Sigma \frac{Q}{t}$ for the given cycle, so this is zero. It is clear that this treatment can be applied to any cycle made up of isothermal and adiabatic lines.

Next consider any reversible cycle, represented by any closed curve. Divide it into steps 13, 35, 57, ..., and draw a zigzag 12345....., in which 12, 34, ... are isothermals, and 23, 45, ... are adiabatics. Then we know that $\int \frac{dQ}{t}$ along the zigzag cycle is zero. In the limit when the steps are infinitesimal the zigzag coincides with the curve. Now $\frac{dQ}{t}$ may be written in the form $\frac{M}{t}dx + \frac{N}{t}dy$, where $\frac{M}{t}$ and $\frac{N}{t}$ are functions of x and y; and this (which is the mathematical expression of the reversibility) shews that $\int \frac{dQ}{t}$ along the zigzag coincides in the limit with $\int \frac{dQ}{t}$ along the curve. Therefore $\int \frac{dQ}{t}$ along the curve, that is to say for any reversible cycle, is zero*.



* Some properties of a curve, for example its length, could not be derived from the limiting case of a zigzag.

Digitized by Google

In fact, if we have a cycle drawn in an area traversed by adiabatic lines, any line which is cut by the cycle from left to right must be cut by it, at some other point of its course, from right to left, and the elements of $\int \frac{dQ}{t}$ corresponding to these two intersections cancel.

As $\int \frac{dQ}{t}$ is zero for every cycle in a diagram in which lines represent reversible processes, the value of this integral between any two points is independent of the route, and $\frac{dQ}{t}$ is the differential of a function of the variables in terms of which the state of the substance is specified. If $\frac{dQ}{t}$ is written in the form $\frac{M}{t}dx + \frac{N}{t}dy$, M and N satisfy the equation $\frac{d}{dy}\left(\frac{M}{t}\right) = \frac{d}{dx}\left(\frac{N}{t}\right)$, see p. 3.

Let us apply this equation to a simple example, to shew how the second law of thermodynamics imposes restrictions on the properties of substances. Suppose that it is known, or assumed, that the internal energy of a certain gas is proportional to its temperature. Then if t and v are taken for variables, the first law of thermodynamics gives $dQ = k\,dt + p\,dv$ for reversible processes, where k is a constant; and the second law gives $\frac{d}{dv}\left(\frac{k}{t}\right) = \frac{d}{dt}\left(\frac{p}{t}\right)$. Thus $\frac{d}{dt}\left(\frac{p}{t}\right) = 0$, that is to say $\frac{p}{t}$ is a function of v only. Accordingly a substance which has the property which has been assumed must have a characteristic equation of the form $\frac{p}{t} = f(v)$. If it should be found that the pressure does not vary so as to be exactly proportional to the temperature, when the substance receives heat at constant volume, the internal energy cannot be proportional to the temperature. A result like this, involving temperature quantitatively, would not be possible if a choice of a scale for temperature had not been made.

26. Historical note. We owe the second law of thermodynamics to Sadi Carnot, whose work was published in 1824. He invented the method of argument derived from a reversible heat engine, and gave the law in a form which may be stated as follows: namely, that the work done by any substance in a Carnot cycle, with an infinitesimal range of temperature, dt, is $\mu Q\,dt$, where Q is the quantity of heat received in the isothermal process of the cycle, and μ

Digitized by Google

depends only on the temperature, and has the same value for all substances. This pointed to the value of μ being an important object for study, both for verification of the theory, and for the purpose of applications of it. (We now define the temperature scale so that $t = J/\mu$.) If work is represented by $p\,dv$, and the state of the substance may be specified by p and v, this result takes a form which may be stated as follows: namely, that the increase of pressure of the substance per unit increase of temperature, at constant volume, is equal to μ times the quantity of heat received per unit increase of volume in a reversible isothermal process. Clapeyron, who in 1834 called attention to Carnot's work, and to the importance of the quantity μ, gave the form which Carnot's result assumes for a mixture of a vapour and its liquid, namely $\mu = \dfrac{V - w}{L}\dfrac{dp}{dt}$, where V and w are the specific volumes of the vapour and liquid respectively, and L is the latent heat. Thus the expression for μ given by this equation has, according to the theory, the same value for all vapours at a given temperature. These statements do not involve any choice of a temperature scale. Before the thermodynamic scale of temperature had been definitely adopted, μ was known as Carnot's function.

Carnot made remarkable progress with the subject, considering that he was working without a theory of energy. He was fully alive to the importance of the question whether the possible efficiency of a heat engine has different values for different working substances, a question to which his theory supplied an answer. He discussed the points on which the efficiency of a heat engine depends, and the importance of a wide range of temperature. In this connection he called attention to various advantages that might be gained by the use of air as the working substance of an engine, instead of steam; one of his points being that air might be heated by an internal combustion.

In 1848 James Thomson provided an important verification of Carnot's theory by predicting that the well known expansion, which takes place when water freezes, would be found to be associated with the freezing point of water being lowered by pressure, although this had never been observed. By an application of Carnot's theory, which was practically equivalent to the use of Clapeyron's formula, he obtained a correct result for the magnitude of the effect. It amounts to about one tenth of a degree centigrade for an additional pressure of $13\frac{1}{2}$ atmospheres.

Digitized by Google

The restatement of the theory of thermodynamics, which brought Carnot's investigations into line with the theory of energy, was mainly the work of Clausius, Kelvin and Rankine, who studied the subject simultaneously. The adoption of a thermodynamic scale of temperature was first proposed by Kelvin. Clausius was mainly responsible for the introduction into physics of the quantity to which he gave the name Entropy.

Digitized by Google

CHAPTER V

ENTROPY

27. Definition of entropy. The result which has been obtained concerns the various states which a given substance can assume, such that any one can be reached from any other by a reversible process. A change from one of these states to another can generally take place reversibly by various routes, and the second law of thermodynamics requires that $\int \frac{dQ}{t}$ should have the same value for all these routes; dQ being the quantity of heat received at temperature t. This result shews that the following scheme may be adopted for expressing the values of this integral for a given substance. Choose a standard state of the substance, denoted by 0, and let ϕ be a quantity which has a certain definite value for each state, namely

$C + \int \frac{dQ}{t}$ for a reversible process from 0 to the state in question.

This quantity, ϕ, is called the entropy of the substance. The constant C, which is the value of the entropy for the state 0, must be chosen arbitrarily for any given substance.

If ϕ_1 and ϕ_2 denote the entropy of the substance for states 1 and 2 respectively, $\int \frac{dQ}{t}$ for a reversible process from 1 to 2 is equal to $\phi_2 - \phi_1$, for it may be calculated by means of a process by which the substance changes from 1 to 0 and then from 0 to 2. This shews that $\frac{dQ}{t}$ for any reversible process is the differential of the entropy.

The equation for a reversible process $dQ = t\,d\phi$, in which ϕ is understood to be a quantity which depends only on the state of the substance, expresses the second law of thermodynamics in a form which is often more convenient than a statement involving an integral.

Digitized by Google

The existence of entropy thus defined, as a property of a given substance in a given state, expresses a characteristic of heat which distinguishes it from energy received by a body in other ways. In any process, reversible or irreversible, when a substance receives heat it gains energy; it may however gain or lose energy in other ways. But if the processes performed by a substance are restricted to being reversible, it gains entropy only when it receives heat, and loses entropy only when it parts with heat; the entropy cannot be altered in any other way, and in an adiabatic process is constant.

A simple process to use for finding the change of entropy, for a given change of state of a substance, is one which consists of an adiabatic process and an isothermal process. The increase of entropy is then the quantity of heat received during the isothermal change divided by the absolute temperature at which this takes place.

28. Irreversible processes. It should be noted that perfect reversibility of a process is an ideal which is never actually attained, though deviations from it may properly be neglected in theory if they are not an essential feature of the process in question, and can be diminished as much as may be desired by proper contrivances, and allowed for in the interpretation of experiments. There are however processes which are, not accidentally, but essentially and frankly irreversible, such as a process in which expansion is not intended to be balanced, or any process in which mechanical friction, or electrical resistance in a conductor, plays an essential part.

The change of entropy which takes place in an irreversible process can be found if a reversible process can be contrived by means of which the same change of state of the substance might be effected. Thus if work is applied to stir a unit mass of water, which is then allowed to come to rest, no heat having been received or parted with, the effect produced is a rise of temperature of the water. Here the same total effect could be produced by a reversible operation, namely by communicating heat to the water. Let c be the specific heat of water, then the quantity of heat received in an elementary step of this process is cdt, and the gain of entropy is $\int \frac{cdt}{t}$. If c can be treated as constant this expression is $c \log \frac{t_2}{t_1}$, where t_1 and t_2 are the initial and final temperatures measured from the absolute zero.

The case of a perfect gas affords simple illustrative examples. For

Digitized by Google

reversible processes the energy equation for a perfect gas is, with v and t for independent variables,

$$\frac{dQ}{t} = k_v \frac{dt}{t} + AR \frac{dv}{v};$$

and with p and v for independent variables

$$\frac{dQ}{t} = k_v \left(\frac{dp}{p} + \gamma \frac{dv}{v}\right).$$

Each of these equations exhibits $\frac{dQ}{t}$ as a perfect differential, and thus shews that the requirements of the second law of thermodynamics are provided for by the properties which define a perfect gas. Writing $t d\phi$ for dQ, we get, by integration of the second equation,

$$\phi = k_v \log_e (pv^\gamma) + C,$$

C being a constant depending on the choice of a zero for entropy. The entropy is constant in a process for which pv^γ is constant, and the increase of entropy as the substance passes from a state 1 to a state 2 is $k_v \log_e \frac{p_2 v_2^\gamma}{p_1 v_1^\gamma}$.

If the gas is compressed adiabatically its temperature is raised, and its energy is increased, without change of entropy. If it undergoes balanced expansion the process is reversed. If however it is permitted to double its volume by unbalanced expansion and then come to rest, without doing work or receiving or parting with heat, entropy is gained. This is an irreversible process; but any number of reversible processes may be contrived which would produce the same total result, the volume doubled without change of temperature. Any line drawn in a diagram from the initial to the final state gives such a process. It may be isothermal balanced expansion, heat being received; or it may be the process represented by a straight line; or it may be a constant pressure process, followed by a constant volume process. The gain of entropy may be calculated from any such process, or may be obtained from the general formula. It is $k_v (\gamma - 1) \log_e 2$.

It is an accepted principle (first enunciated by Clausius), that for any cycle in which a substance receives heat dQ per unit mass at temperature t, $\int \frac{dQ}{t}$ is either zero or negative. It is zero in the ideal case of a reversible process. And when irreversible operations occur, which can be examined, they are found to involve something which

Digitized by Google

produces the same total effect as receiving heat, and thus tends to decrease the value of $\int \frac{dQ}{t}$ for the cycle. Also the theory of the Carnot engine shews that, for any small change in a substance which can be produced by an elementary step of a reversible process, and may also be produced by an irreversible process without finite change of temperature, $\frac{dQ}{t}$ is less than the increment of entropy, if it is not equal to it.

Let the change in question be from a state 1 to a state 2; and suppose that a positive quantity, δq, of heat per unit mass, is received in the reversible step 12, and a different positive quantity, δh, when the change from 1 to 2 is made in some irreversible way. Let us now suppose that the two engines, whose performances are compared on page 38, have cycles which are identical except in two respects, namely (i) that in the Carnot engine the working substance receives heat by the reversible step 12, while in the other engine it receives heat by the irreversible step 12; and (ii) that the Carnot engine uses unit mass of the substance, while the irreversible engine uses a mass m, adjusted so that the amounts of work done in the two cycles may be equal. In the limit when the reversible step 12 is infinitesimal, the fact that it is not isothermal is immaterial. It has been shewn on page 38 that, if $\delta q'$ is the quantity of heat parted with per unit mass of the substance at the lower temperature, $m\delta h$ and $m\delta q'$ are equal respectively to $\delta q + \lambda$ and $\delta q' + \lambda$, where λ is a positive quantity. Thus $\frac{\delta h}{\delta q'}$ is equal to $\frac{\delta q + \lambda}{\delta q' + \lambda}$, and this is less than $\frac{\delta q}{\delta q'}$; therefore $\delta h < \delta q$.

It may be shewn, in a similar manner, that if δq and δh are respectively positive quantities of heat parted with in an elementary change, performed reversibly and irreversibly, and are not equal, $\delta h > \delta q$. Also the case of heat being parted with in the reversible step and received in the equivalent irreversible one, is inadmissible, for this would give an irreversible cycle in which only positive quantities of heat are received, and it is all realised as work. So it has been proved that any alteration of $\int \frac{dQ}{t}$ for a reversible process, due to an elementary step of it, or any number of such steps, being replaced by equivalent irreversible steps, is a decrease; and that any such alteration of it for a cycle makes it negative.

Any change that can be traced in the entropy of a substance, due

Digitized by Google

to a process in which it does not receive or part with heat, must be an increase; because $\int \frac{dQ}{t}$ for the actual process is zero, so $\int \frac{dQ}{t}$ for an equivalent reversible process must be greater than zero.

29. Equations for reversible processes. The equations which express the theory of reversible processes, taking pdv as the expression of work, may be written

$$td\phi = dE + Apdv,$$
$$dQ = td\phi.$$

Taking a diagram in which lines represent reversible processes, the entropy of the substance has a single definite value for each point of the diagram. Its values may be tabulated, or they may be represented by ordinates erected at right angles to the diagram, at every point of it, tracing out a surface. The adiabatic lines of the diagram are the contour lines of this surface. The value of the entropy provides a numerical specification for these lines, as temperature does for isothermal lines. It is clear that the value of $t\frac{d\phi}{dt}$ for any given process is the specific heat for that process, see p. 20.

It is often useful to take entropy as one of the independent variables in terms of which the state of the substance is specified, and as one of the coordinates in a diagram, in conjunction, for example, with specific volume, or temperature, or the quantity which has been denoted by I. The use of a v, ϕ diagram has certain advantages, and is suggested by the equation $dE = td\phi - pdv$ (using the work unit for heat). Willard Gibbs derived from this his famous thermodynamic surface, which is the surface traced out by erecting ordinates representing E at all points of a v, ϕ diagram. The equation shews that the slope of a section of this surface by a plane at right angles to the axis of v (giving a constant volume process) is equal to t; and that the slope of a section by a plane at right angles to the axis of ϕ (giving an adiabatic process) is equal to $-p$. The surface shews in an instructive way the relations between the solid, liquid and vapour states of a substance.

The most useful diagram however is that in which entropy is combined with temperature. In an entropy temperature diagram the adiabatic and isothermal lines are straight lines parallel to the axes. Another important feature of this diagram is that it exhibits the quantity of heat received by the substance, in any process, in the form

Digitized by Google

of an area bounded by the line representing the process, in the same way that work is represented by an area in a p, v diagram. This follows from the formula $dQ = t\,d\phi$, which is analogous to the formula for work $dW = p\,dv$. The way in which signs are to be attached to areas, in order that they may represent the values of such an integral as $\int t\,d\phi$ for a given process, has already been discussed, p. 2.

For a cycle the net quantity of heat received is equal to the net amount of work done, if the same unit is used for heat and work. If the work unit is used for heat, $\int t\,d\phi$ is equal to $\int p\,dv$ for the cycle; and the area enclosed by the line representing the cycle in a t, ϕ diagram is equal to the area enclosed by the corresponding line in a p, v diagram. It is convenient to draw the diagrams so that the axes of t and p point north when the axes of ϕ and v point east. Then for a given cycle the circuits in the two diagrams are described the same way round; and the heat or work, as the case may be, is represented by a positive area in the case in which the process traces out the circuit clockwise. The usual practice is to reckon heat and entropy in terms of a thermal unit; so the equation usually occurs in the form $\int t\,d\phi = A \int p\,dv$, and the area in the t, ϕ diagram is A times the area in the p, v diagram. The factor A is to be omitted if the work unit is used for heat, and whether it is or is not inserted in theoretical formulae is unimportant.

The existence of an entropy temperature diagram expresses the second law of thermodynamics, and is often the most convenient way of expressing it.

30. A vapour and its liquid. The case of a saturated vapour and its liquid is one in which the use of the entropy temperature diagram is very convenient. It is also one in which entropy can be tabulated concisely, for it is sufficient to have a table giving the values of the entropy for the vapour alone, and for the liquid alone, for given temperatures.

The p, v diagram of a liquid is nearly confined to a single line, nearly parallel to the axis of p; but it is really contained in a narrow strip of area, with a width depending on the expansion of the liquid with rise of temperature at constant pressure. If a relation is given between the temperature and the pressure, for instance that the pressure for a given temperature is to be that of saturated vapour for that temperature, we get a definite process, and a single line exactly. If, as is nearly true, the specific heat, c, of a liquid depends only on the temperature, the entropy depends only on the temperature, its

Digitized by Google

value at the temperature t_1 being $\int_{t_0}^{t_1} \frac{c\,dt}{t}$, where t_0 is the temperature at which the entropy is taken to be zero. Practically this may be assumed to be the case, and the t, ϕ diagram for a liquid may be regarded as confined to a single line; but actually it occupies a narrow strip of area, the width depending on the variation of entropy with pressure for constant temperature. The relation of this width to that of the strip in the p, v diagram is indicated by the first of the thermodynamic relations given on p. 56. If the pressure of the liquid is given to be that of saturated vapour at the same temperature a definite process is defined, represented by an accurate line. The entropy of the liquid (at this pressure if account is to be taken of the pressure) is denoted by ϕ_w; it is approximately equal to $c \log \frac{t}{t_0}$ for a temperature t, because the variation of c with the temperature is small.

In complete evaporation of a unit mass of the substance, at constant temperature and pressure, it receives heat L (the latent heat); thus its entropy in the state of saturated vapour at temperature t is $\phi_w + \frac{L}{t}$; this is denoted by ϕ_s. In partial evaporation to dryness q the substance receives heat qL; thus the entropy of wet vapour of dryness q is $\phi_w + \frac{qL}{t}$, that is to say $q\phi_s + (1-q)\phi_w$. From tables of ϕ_w and ϕ_s, which depend only on the temperature, the entropy of wet vapour of any given dryness can readily be found. In an adiabatic process the entropy is constant; so if wet vapour undergoes balanced adiabatic expansion from a state P, at temperature t and given dryness q, to a state P', at temperature t' and dryness q', we have an equation which gives the value of q' for a given temperature, namely

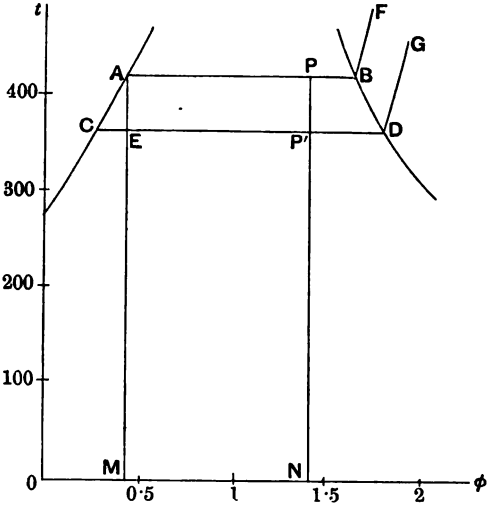
$$q'\phi_s' + (1-q')\phi_w' = q\phi_s + (1-q)\phi_w,$$

provided that the values of the entropy of liquid and vapour can be obtained from tables or otherwise.

In an entropy temperature diagram the liquid line expressing the relation between ϕ_w and t, and the saturated vapour line expressing the relation between ϕ_s and t, may be drawn. Points between these lines represent wet vapour. The ϕ axis must be at the absolute zero of temperature; the position of the t axis depends on the choice of a zero for entropy. Any rectangle with sides parallel to the axes, such as $APP'E$, represents a Carnot cycle. In the figure, which is drawn to

Digitized by Google

represent the typical case of steam and water, AC is the water line, and B, D are points for the same temperatures on the saturated steam line. The dryness of the substance in the state P, in the line AB, is equal to $\frac{AP}{AB}$. Steam, wet or dry, has the property of having its temperature reduced by adiabatic expansion. The area $APP'E$ represents the net amount of heat received in the cycle, that is to say the work done; and the diagram exhibits to the eye the efficiency $\frac{t-t'}{t}$ of a Carnot cycle, since the area $APNM$ represents the heat received at temperature t, and the area $EP'NM$ the heat



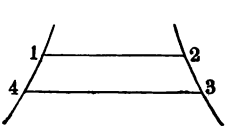
parted with at temperature t'. It also exhibits to the eye the general character of the way in which variations in the form of a cycle affect its efficiency; and facilitates calculations, such, for example, as the calculation of the efficiency of the Rankine cycle $APP'CA$. The fact that the slope of the saturated steam line is negative is to be noted. This implies that the specific heat of saturated steam, for a process following the steam line, is negative, this specific heat being $t\frac{d\phi_s}{dt}$. That is to say, if the temperature of saturated steam is reduced by a reversible process, heat must be supplied to it if the state of saturation is to be maintained. In adiabatic expansion condensation occurs.

Digitized by Google

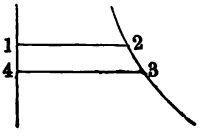
Points representing superheated steam lie beyond the saturated steam line in the t, ϕ diagram. A constant pressure line has the form ABF, or CDG rising steeply beyond BD. For steam the slope beyond BD is about twice that of the water line at the same temperature, because the ratio of specific heats is about 0·5.

Liquid and saturated vapour lines may also be drawn on a p, v diagram, the former close to the axis of p, the latter a curve with negative slope. Between these lines the substance is a mixture of liquid and vapour, and the straight lines of constant pressure are isothermals. The length of such a line is $V - w$, where V is the specific volume of saturated vapour, and w that of the liquid.

The relation between the physical quantities involved in evaporation, which is given by the second law of thermodynamics, is called Clapeyron's equation. It can be derived from the general thermodynamic relations given on p. 56; but it can be obtained more easily by direct reference to the simplest cycle which can be contrived, which



t, φ diagram



p, v diagram

involves evaporation. Consider the cycle 1 2 3 4 1, consisting of complete evaporation at one temperature, a drop of temperature of the substance as saturated vapour, complete condensation at the lower temperature, and a rise of temperature of the substance, as liquid, to its initial value. The area enclosed by the cycle in the t, ϕ diagram is equal to the net amount of heat received, and the area enclosed by the cycle in the p, v diagram represents the equivalent amount of work done. Suppose the two strips of area to be of infinitesimal width, the corresponding intervals of temperature and pressure being dt and dp respectively. The lengths of the strips are $\frac{L}{t}$ and $V - w$ respectively; and the corresponding areas are $\frac{L}{t}\,dt$ and $(V - w)\,dp$. The former is A times the latter, so we obtain the equation

$$A\,(V - w)\frac{dp}{dt} = \frac{L}{t}.$$

This equation may be used for the calculation of the values of whichever

Digitized by Google

of the quantities involved is given with least certainty by direct measurement. If all the quantities are measured it serves as a test of the theory. It may be applied to melting as well as to evaporation. The same two strips of area would be given by a Carnot cycle, in the limiting case in which the widths of the strips are infinitesimal, because the slopes of the two ends of the strips do not affect the result. In this case no direct reference to entropy is necessary; the efficiency of the cycle is $\frac{dt}{t}$, so the work done is $\frac{dt}{t} L$ in thermal units.

Let c be the specific heat of the liquid, and c' that of the vapour subject to the condition of being dry and saturated; then since $\phi_s - \phi_w = L/t$, we get by differentiation with regard to t

$$c - c' = \frac{L}{t} - \frac{dL}{dt}.$$

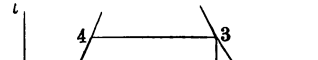
It may be worth while to notice, and is fairly obvious, that the equation

$$A(V-w)\frac{dp}{dt} = \frac{dL}{dt} + c - c'$$

does not involve the second law of thermodynamics.

31. Cycle with irreversible step. If a process which is otherwise reversible contains an irreversible step, only the reversible portion of it can be represented by a line in a diagram, and there is a gap in the line where the irreversible step occurs.

Such a step occurs in the cycle performed by the working substance of a vapour compression refrigerating machine. Let 12341 represent this cycle, in an entropy temperature diagram, for the case in which complete condensation from the state of dry saturated vapour occurs at the higher temperature; the gap in the diagram being between 4 and 1. The step 12 represents isothermal expansion, at the lower temperature, during which the substance takes heat Q from a cold body, and is partially evaporated; 23 represents adiabatic compression completing the evaporation; 34 represents isothermal compression at the higher temperature, during which the substance parts with heat Q'; and 41 is an irreversible step consisting of adiabatic expansion of the substance through a valve,



Digitized by Google

by which it is throttled, to the initial pressure, while the temperature is also adjusted by partial evaporation to the value which corresponds to that pressure. This step cannot be represented by any line, but the state 1 is connected with the state 4 by having the same value for I, and may accordingly be determined.

Let 5 and 6 represent liquid and dry saturated vapour at the lower temperature; and suppose the entropy and the value of I for each of the states 3, 4, 5, 6 to be known from tables, these being saturated vapour and liquid states. The values of the dryness at 1 and 2 are given by

$$q_1 I_6 + (1 - q_1) I_5 = I_4,$$

$$q_2 \phi_6 + (1 - q_2) \phi_5 = \phi_3,$$

since ϕ_2 is equal to ϕ_3. Now the isothermal processes are also constant pressure processes; so the quantity of heat received in an isothermal process, such as 51, which is expressed by $t_1(\phi_1 - \phi_5)$, is also equal to $I_1 - I_5$. Thus

$$Q = t_1(\phi_2 - \phi_5) - (I_1 - I_5) = t_1(\phi_3 - \phi_5) - (I_4 - I_5),$$

$$Q' = t_3(\phi_3 - \phi_4) = I_3 - I_4.$$

The amount of work required for a cycle can be found from a p, v diagram, and is equal to $I_3 - I_2$, see p. 24. This work must be provided from an external source of power. Now $I_2 - I_5$ is equal to $t_1(\phi_2 - \phi_5)$, thus the amount of work is

$$I_3 - I_5 - t_1(\phi_3 - \phi_5).$$

These results give the performance of the machine.

32. Thermodynamic relations. Though a direct comparison of the areas enclosed by a cycle in a t, ϕ diagram, and in a p, v or other equivalent diagram, is often the most convenient way of applying the theory in particular cases, the following general equations may also be used. They express the comparison of areas in the form of four results which are called the thermodynamic relations. These are alternative statements, that is to say from any one of them the other three may be deduced.

The two areas, representing $\int t\,d\phi$ and $\int p\,dv$ for a cycle, may also be expressed by $-\int \phi\,dt$ and $-\int v\,dp$ respectively. The negative signs are needed to make a positive area correspond to a clockwise circuit, and in accordance with the formula $t\,d\phi = d(t\phi) - \phi\,dt$. Thus the relation

Digitized by Google

between the areas enclosed by the circuits in the two diagrams is expressed by any one of the four equations

$$\int (\phi dt - Avdp) = 0,$$
$$\int (td\phi + Avdp) = 0,$$
$$\int (\phi dt + Apdv) = 0,$$
$$\int (td\phi - Apdv) = 0,$$

each of which is true for any reversible cycle. Accordingly the four expressions inside these integrals are all perfect differentials; the fourth, for example, being the differential of E, the energy. Thus the first of these equations is equivalent to the statement that, if ϕ and v are expressed as functions of t and p, $\frac{d\phi}{dp}$ is equal to $-A\frac{dv}{dt}$. Here $\frac{dv}{dt}$ is the rate of increase of volume with rise of temperature at constant pressure. Let us write this in the form $\left(\frac{dv}{dt}\right)_p$, the suffix p indicating that the expansion is for a constant pressure process. This notation is analogous to the notation k_v and k_p for specific heats for constant volume and constant pressure processes. A corresponding result is obtained from each of the other three equations. Thus

$$\left(\frac{d\phi}{dp}\right)_t = -A\left(\frac{dv}{dt}\right)_p \quad \text{.....(1),}$$

$$\left(\frac{dt}{dp}\right)_\phi = A\left(\frac{dv}{d\phi}\right)_p \quad \text{.....(2),}$$

$$\left(\frac{d\phi}{dv}\right)_t = A\left(\frac{dp}{dt}\right)_v \quad \text{.....(3),}$$

$$\left(\frac{dt}{dv}\right)_\phi = -A\left(\frac{dp}{d\phi}\right)_v \quad \text{.....(4).}$$

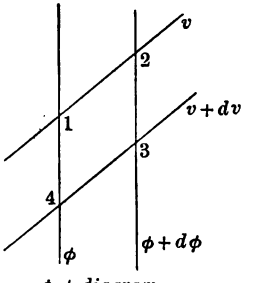
If entropy is measured in terms of the work unit the factor A is to be omitted in each case.

These four equations are the thermodynamic relations. The third of them should be compared with the verbal statement of Carnot's theory on p. 43. The fourth gives a relation between the increase of temperature of an elastic substance in adiabatic expansion, and its increase of pressure when it receives heat at constant volume. If the former is negative the latter must be positive, and *vice versa*. Thus if a substance is found with the exceptional property

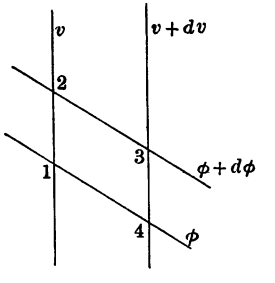
Digitized by Google

of being cooled by adiabatic compression, the laws of thermodynamics require that its pressure should decrease when it receives heat at constant volume. The rate of this decrease as it receives heat is $1/At$ times the former rate of cooling as its volume is decreased.

The thermodynamic relations may be obtained geometrically by inspection of elementary areas enclosed by corresponding circuits in the two diagrams. For the first relation the areas must be those bounded by a pair of isothermal lines for temperatures t and $t+dt$, and a pair of constant pressure lines for the pressures p and $p+dp$. For the second relation they must be bounded by a pair of adiabatic lines and a pair of constant pressure lines. For the third relation they must be bounded by a pair of isothermal lines and a pair of constant volume lines. For the fourth relation they must be bounded by a pair of adiabatic lines and a pair of constant volume lines. Attention must be paid to the signs, which are settled by the fact that the lines must be drawn so that two corresponding circuits are traversed the same way round. The figure shews the diagrams for the fourth relation.



t, φ diagram



p, v diagram

The scale is so large that the lines are straight. The area enclosed by the cycle 12341 in the t, ϕ diagram is the product of $-\left(\frac{dt}{dv}\right)_\phi dv$ (that is to say the length 41) and $d\phi$; and the area enclosed by the same cycle in the p, v diagram is the product of $\left(\frac{dp}{d\phi}\right)_v d\phi$ (that is to say the length 12) and dv.

33. Characteristic equations and specific heats. The general relations between physical quantities, which are provided by the second law of thermodynamics, are very important. The most famous example of such a relation is Clapeyron's equation, which is

Digitized by Google

a particular application of the third thermodynamic relation. These relations indicate the character of the results which may be obtained. But they take a great variety of particular forms, each appropriate to some reversible physical or chemical process which happens to be under consideration, involving either a quantity of heat or adiabatic change. Thus we may expect any physical quantity which, like latent heat or specific heat, represents a quantity of heat defined by some reversible process, to be connected by the second law of thermodynamics with the quantities which express the work done by a substance, or with the form of its characteristic equation.

Accordingly a characteristic equation for a given substance has not merely to satisfy the condition of fitting the values of p, v and t, experimentally determined for a certain range of states of the substance, with reasonable accuracy. It is not to be regarded as sound unless it satisfies tests imposed by the laws of thermodynamics, which may involve two differentiations of the equation. The importance of Calendar's characteristic equation for steam is partly derived from the satisfactory extent to which it stands such tests.

Let us use the second law of thermodynamics to revise the form of the equation for the heat received by a substance during a reversible process. Take t and v for independent variables, specifying the state of the substance, and write k_v and k_p for the specific heats at constant volume and at constant pressure. The equation may be written

$$dQ = k_v dt + N dv.$$

Here N is $t\left(\frac{d\phi}{dv}\right)_t$, and this by the third thermodynamic relation is equal to $At\left(\frac{dp}{dt}\right)_v$; thus the equation is

$$dQ = k_v dt + At\left(\frac{dp}{dt}\right)_v dv.$$

Similarly, if t and p are taken as independent variables,

$$dQ = k_p dt - At\left(\frac{dv}{dt}\right)_p dp.$$

These two equations give respectively

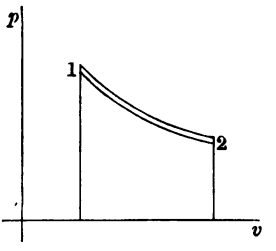
$$\frac{1}{t}\left(\frac{dk_v}{dv}\right)_t = A\left(\frac{d^2p}{dt^2}\right)_v \text{ and } \frac{1}{t}\left(\frac{dk_p}{dp}\right)_t = -A\left(\frac{d^2v}{dt^2}\right)_p,$$

as expressions of the fact that $\frac{dQ}{t}$ is a perfect differential.

These results could be obtained from first principles, without

Digitized by Google

quoting the thermodynamic relations. Consider the Carnot cycle in which the two isothermal processes practically coincide, being at temperatures t and $t+dt$. The work done is represented in a p,v diagram by the area of a strip 12, of infinitesimal width, between consecutive isothermal lines. This area is $\int_{v_1}^{v_2} \delta p\, dv$, where δp is its width parallel to the axis of p. The quantity of heat received in the isothermal process 12 is $\int_{v_1}^{v_2} N dv$, and the efficiency of the cycle is $\frac{dt}{t}$. Thus $A\int_{v_1}^{v_2} \delta p\, dv = \frac{dt}{t}\int_{v_1}^{v_2} N dv$; and as this is true for any given portion of an isothermal line, $A\,\delta p$ is equal to $\frac{dt}{t}N$. Now $\delta p = \left(\frac{dp}{dt}\right)_v dt$, therefore $N = At\left(\frac{dp}{dt}\right)_v$, as before.



The equation thus obtained shews that the specific heat for any given process is equal to

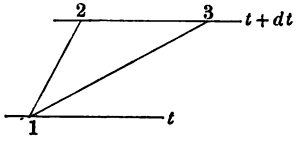
$$k_v + At\left(\frac{dp}{dt}\right)_v \frac{dv}{dt},$$

where $\frac{dv}{dt}$ is the rate of increase of v, compared with that of t, for the process in question. Take a constant pressure process, we then get

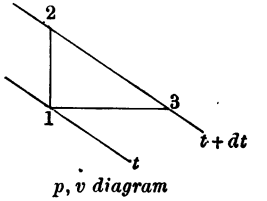
$$k_p - k_v = At\left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dt}\right)_p.$$

Thus if the characteristic equation of the substance is known, $k_p - k_v$ is known in terms of p, v and t.

This relation between specific heats can be obtained independently by a comparison of the areas enclosed in the t, ϕ and p, v diagrams by a suitably chosen cycle. Draw in each diagram a cycle 1231, such



t, φ diagram



p, v diagram

Digitized by Google

that 12 is an elementary step at constant volume from a temperature t to a temperature $t+dt$, and 23 is an elementary isothermal step to a point 3, such that 31 will complete the cycle at constant pressure. The relation between the areas of the triangles gives

$$(\phi_3-\phi_2)\,dt = A\,(p_2-p_1)\,(v_3-v_1).$$

Now $$\phi_3-\phi_1=\frac{k_p\,dt}{t}, \text{ and } \phi_2-\phi_1=\frac{k_v\,dt}{t};$$

also $$p_2-p_1=\left(\frac{dp}{dt}\right)_v dt, \text{ and } v_3-v_1=\left(\frac{dv}{dt}\right)_p dt;$$

so we get, as before, $$\frac{k_p-k_v}{t}=A\left(\frac{dp}{dt}\right)_v\left(\frac{dv}{dt}\right)_p.$$

If a substance has the characteristic equation $pv=Rt$, where R is a constant, $\left(\frac{dp}{dt}\right)_v$ is equal to $\frac{p}{t}$; and we get the energy equation

$$dQ=k_v\,dt+Ap\,dv.$$

But this equation may also be written $dQ=dE+Ap\,dv$, or

$$dQ=\frac{dE}{dt}\,dt+\frac{dE}{dv}\,dv+Ap\,dv;$$

therefore $\frac{dE}{dv}$ is zero. That is to say the second law of thermodynamics shews that, if a substance has the characteristic equation $pv=Rt$, its internal energy is a function of the temperature only. The second of the properties assumed (p. 27), as defining a perfect gas, is thus derivable from the first, and is not independent of it. We have also $k_p-k_v=AR$, so that k_p as well as k_v is a function of the temperature only. But, without further assumption, k_v and k_p are not necessarily constant. Thus the observed increase of the specific heats of gases, at high temperatures, is not inconsistent with the equation $pv=Rt$. The adiabatic equation for a perfect gas depends on the specific heats being constant; and this equation assumes a different form for a gas, with characteristic equation $pv=Rt$, whose specific heats are not constant.

34. Electromotive force of a storage battery. The action of a storage battery affords a familiar example of an approximately reversible operation, involving internal energy and heat, in which electrical work is done. In order that the action may be treated as reversible, the dissipation of energy which is due to the electrical resistance of a cell, and is proportional to the square of the electric

Digitized by Google

current passing through it, must be neglected. This effect has no value which is essential to the working of a cell, and we may suppose that by suitable arrangements it may be diminished as much as may be desired. Thus the neglect of it is analogous to the neglect of friction in the theory of an action involving mechanical work. Allowance must be made for it in any actual measurements. In the practical working of a cell other unessential complications occur which cause irregularities. Apart from these, the theory of the action of the ordinary form of cell of a storage battery may be stated as follows.

A cell consists of plates of lead and lead peroxide, immersed in dilute sulphuric acid. If the terminals of the cell are joined to an electric motor, an electric current passes through the system doing electrical work, while a portion of the lead and lead peroxide and sulphuric acid is changed into lead sulphate and water in accordance with the formula

$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O^*.$$

The substance which undergoes this chemical change may be called the working substance of the cell. Initially it consists of lead, lead peroxide and sulphuric acid in the proportions given by the left-hand side of the formula; finally it consists of lead sulphate and water in the proportions given by the right-hand side of the formula. Denote these two states of the substance by A and B; then at any intermediate stage of the process a unit mass of the working substance consists of a certain mass x in the state B, and a mass $1-x$ in the state A. The quantity of electricity which has passed through the system, in the positive direction of the current, at this stage of the process is proportional to x, and will be denoted by q. The state of the working substance at any instant is specified by x and the temperature, t. The electromotive force between the terminals of the cell is practically independent of the magnitude of the current so long as this is not too great, but varies to some extent with the temperature of the substance. Let this electromotive force, taken so as to be positive, be denoted by e.

During this process, which is called the discharge of the cell, the temperature of the working substance tends to fall. That is to say in an isothermal process the substance absorbs heat. The large quantity of liquid electrolyte in a cell prevents any great variations

* There is not yet complete agreement as to the changes which take place in a cell; but this formula represents what is usually stated.

Digitized by Google

of temperature. Let H be the excess of the internal energy of A per unit mass over that of B at the same temperature. The amount of electrical work done by the substance is slightly greater than H, the difference representing the quantity of heat received together with the energy value of the change of temperature.

The energy which the cell has lost, in a process of discharge, may be restored to it by passing an electric current through it in the reverse direction by means of a dynamo. By this operation the cell is said to be charged. The chemical action is reversed, restoring the working substance to its initial state. The temperature of the substance tends to rise, and if the process is isothermal, heat is parted with. If the current and the flow of heat are regulated so as to reverse the previous action, following any fluctuations which occurred in the discharge, a process of charge will be produced which is exactly the reverse of the process of discharge.

Thus the increase of the entropy of the substance in the process described, direct or reversed, is measured by $\int \frac{dQ}{t}$, where dQ is the quantity of heat received at the temperature t. That is to say we have the equation $td\phi = dQ$. Any such process is represented by a line in a t, ϕ diagram, in which quantities of heat received are represented by areas.

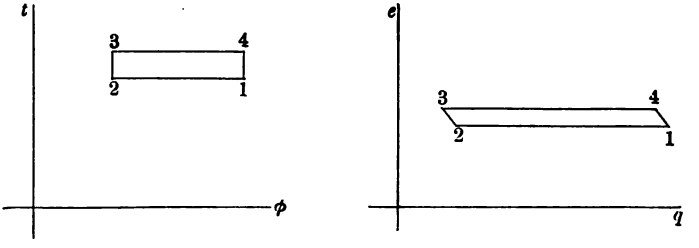
The state of the substance may also be specified by e and q, since these two quantities determine t and x respectively. Now edq is the amount of electrical work done by the substance in an elementary step of a process; thus in an e, q diagram, amounts of electrical work done are represented by areas, in the same way that amounts of mechanical work done in the expansion of a fluid are represented by areas in a p, v diagram.

In any cycle the internal energy of the substance is on the whole unchanged, and the net amount of heat received is equal to the net amount of work done. That is to say, if heat is measured in electrical work units, the areas enclosed by the circuits in the t, ϕ and the e, q diagrams are equal. This fact is completely expressed by a comparison of the areas for the case of a Carnot cycle with an infinitesimal range of temperature dt, and a corresponding infinitesimal range of electromotive force de. In an isothermal process of discharge the substance is doing work and receiving heat; q and ϕ are both increasing. This shews that in an adiabatic process $\frac{de}{dt}$ is positive, because the circuits in

Digitized by Google

the two diagrams must be traversed the same way round when the axes of e and q are taken parallel to the axes of t and ϕ respectively.

Denote the Carnot cycle by 12341; 12 being an isothermal process of charge at the temperature t, 23 an adiabatic step of charge



by which the temperature is raised to $t + dt$, 34 an isothermal process of discharge, and 41 an adiabatic step of discharge by which the cycle is completed. Let Q_1 be the quantity of heat received in isothermal discharge, per unit mass of the substance undergoing change, and q_1 the corresponding quantity of electricity which passes. In the isothermal processes e is constant, thus in each diagram the area is a narrow strip between straight lines; and if heat is measured in electrical work units, and m is the mass dealt with, the areas are $m\frac{Q_1}{t}dt$ and mq_1de respectively, so that we get the equation $Q_1 = tq_1\frac{de}{dt}$. Now eq_1 is equal to $H + Q_1$, thus

$$e = \frac{H}{q_1} + t\frac{de}{dt}.$$

$\frac{H}{q_1}$ is known from chemical data, and e and $\frac{de}{dt}$ can be determined by measurements of the electromotive force at various temperatures. This equation may therefore be verified, and this has been done with satisfactory results. Under ordinary conditions e represents about two volts, and $t\frac{de}{dt}$ represents about one-tenth of a volt.

Digitized by Google

CHAPTER VI

ENTROPY OF A SYSTEM

35. Entropy of a system. The entropy of a substance has been defined with reference to a unit mass of a substance. This quantity, which has been denoted by ϕ, might, if we needed a more precise terminology, be called the specific entropy of the substance. It is analogous to specific volume, or to the energy of a substance reckoned per unit mass. But the term entropy has also a wider application, corresponding to the use of the term energy. Thus the entropy of a body, or of a system, means the sum of the specific entropies of its parts each multiplied by the mass of that part. These parts must be small enough for each to be treated for the purpose of calculations as having a definite specific entropy. We might, if it was necessary to be more precise, call the entropy of a whole body, or system, its total entropy. In the case of volume the terminology which is used distinguishes between specific volume and total volume. But in the case of entropy, as well as that of energy, the corresponding distinction is generally supplied sufficiently by the context.

Irreversible operations, which diminish the availability of the energy of a system for doing work, increase its entropy. If an isolated system, so protected that it cannot receive or part with heat, undergoes changes, its entropy cannot decrease, but may and generally does increase. From this is drawn the inference, which has important applications, that if the entropy of such a system has reached a maximum value, the system is in a state of equilibrium.

Consider first the case in which the changes in a system, isolated in this way, are perfectly reversible. The total entropy is then constant, because no change of entropy occurs in any part of it without heat being received or parted with, and any direct transfer of heat that takes place must occur between bodies at the same temperature, so that one of them gains the same amount of entropy that the other

Digitized by Google

loses. A direct transfer of heat between two bodies of the system at different temperatures is an irreversible operation.

Irreversible changes within a substance, at uniform temperature, have already been considered. They cause an increase of entropy, apart from that due to heat being received, or at any rate cannot decrease it. Besides these effects, it is unavoidable that in any system which is not at uniform temperature, direct passage of heat between bodies at different temperatures should occur; and it can be shewn that this increases the entropy of the system. The transfer takes place from a body at a higher to a body at a lower temperature. Let A and B be two bodies of the system at absolute temperatures t and t' respectively. If a quantity of heat Q passes from A to B, and is small enough not to affect their temperatures, A loses an amount of entropy equal to $\frac{Q}{t}$, and B gains an amount equal to $\frac{Q}{t'}$. Thus the system consisting of A and B gains an amount of entropy equal to $Q\left(\frac{1}{t'}-\frac{1}{t}\right)$, and this is positive. Any direct passage of heat between two bodies at different temperatures diminishes the amount of mechanical work that can be obtained from the system; for it tends to equalise temperatures, and this involves a loss of an opportunity of doing work by means of an engine performing cycles, which might employ one of the bodies as a source of heat, and the other as a sink. This is expressed by the fact that the entropy is increased.

Conduction of heat in a body may be said to generate entropy. The production of entropy does not however necessarily take place at a point at which there is conduction of heat. Steady conduction of heat does not affect the entropy of a body in which it occurs. A particle A parts with heat to a particle B at a lower temperature, and this transfer by itself would increase the entropy of the body. But in steady conduction each of the particles loses the same quantity of entropy that it gains; and the fact that A's quantity is less than B's quantity does not affect the entropy of the body. In the case of a steady passage of heat through a boiler plate, the water gains more entropy than the furnace gases lose. But a generation of entropy in the boiler plate occurs only if the quantities of heat received and parted with by some particle of it differ. Moreover entropy cannot be treated as flowing through the plate, in the way that heat or a fluid flows.

Digitized by Google

36. Availability of heat. Let a body A part with a quantity of heat dQ at a point at which the temperature is t, so that its entropy is diminished by $\frac{dQ}{t}$. Let a working substance be employed to receive this heat, and to produce mechanical work from the energy which this heat represents, without aid from any permanent change in its own state, that is to say, with the condition that the substance goes through a cyclical process. We know that the greatest amount of work which can be produced in this way is that which is obtained when the cyclical process employed is a Carnot cycle, in the course of which the working substance parts with heat at the temperature of the coldest body that can be found to receive it. Call this body B, and let its temperature be t_0. The amount of work produced is $dQ\left(1-\frac{t_0}{t}\right)$; that is to say, that amount of the energy parted with by A which is necessarily unavailable for the production of mechanical work, is t_0 times the amount of entropy lost by A. Also B receives a quantity $\frac{t_0}{t}dQ$ of heat; that is to say, if it is not undergoing any irreversible change, its entropy is increased by $\frac{dQ}{t}$, the same amount as is lost by A. As the working substance has suffered no change let us leave it out of account, and confine our attention to the system consisting of A and B, the only bodies that have undergone any change. A has parted with heat and lost a certain amount of entropy; B receiving heat has gained the same amount of entropy; and the greatest amount of work that can be obtained from the heat supplied by A has been produced.

In a system of bodies in which the temperature is not uniform, the distribution of temperature may be altered by means of Carnot engines working between the different parts of the system, until the temperature has been equalised throughout it. If no part of the system receives or parts with energy except by receiving or parting with heat, and there is no irreversible change, each part goes through a definite process during a given change of its temperature, and the amount of work done in the operation of equalising the temperature may be calculated. The final uniform temperature may be found from the fact that the entropy of the system is unchanged, and thus this temperature has a definite value however the operation may be arranged. If t_1 is the initial

Digitized by Google

temperature of some portion of the system, the increase of entropy of this portion is $\int_{t_1}^{t_2} \frac{dQ}{t}$, dQ being an elementary quantity of heat received by it, and t_2 the final temperature of the whole system. Thus if Σ denotes summation for the different portions into which the system is divided, the equation for t_2 expressing the fact that the entropy of the system is unchanged is $\Sigma \int_{t_1}^{t_2} \frac{dQ}{t} = 0$, and the amount of work done is $-\Sigma \int_{t_1}^{t_2} dQ$.

Denote by A those portions of the system of which the initial temperature is greater than t_2, and by B those portions of the system of which the initial temperature is less than t_2. A parts with heat, and the energy which this represents is partly realised as work, the balance being received as heat by B. But the operation may be described in another way by the introduction into the system of a neutral body C, at constant temperature t_2, which undergoes no change, and parts with heat as fast as it receives it. The operation may be imagined to be conducted by means of a Carnot engine working between A and C, and another working between C and B, both doing work. The work done by the first engine is equal to the amount of heat parted with by A less t_2 times A's loss of entropy; and the work done by the second engine is equal to t_2 times B's gain of entropy less the amount of heat received by B. The amount of work done in this way is the greatest amount of work which a system can do, during a process in which its temperature is equalised, provided that it is not able, or is not permitted, to do work except by passage of heat.

We may have an inert substance like water, assumed to have constant specific volume, and no choice of processes by which to pass from one temperature to another. Take a system consisting of two quantities of such a substance, with constant specific heat k, the temperatures of the two quantities being initially t_1 and t_1', and their masses m and m'. The final common temperature, t_2, is given by the equation which expresses that there is no change of entropy. This equation is

$$m \log \frac{t_2}{t_1} + m' \log \frac{t_2}{t_1'} = 0,$$

that is to say, $t_2^{m+m'} = t_1^{m} t_1'^{m'}$; and the work done is

$$km\,(t_1 - t_2) - km'\,(t_2 - t_1').$$

This is the greatest amount of work that can be obtained from the

Digitized by Google

system, assuming that it has no kinetic energy, and neglecting forces such as gravitation between the parts of it. If m and m' are equal, t_2 is equal to $\sqrt{t_1 t_1'}$, and the amount of work done is

$$km\,(t_1 + t_1' - 2\sqrt{t_1 t_1'}).$$

If the temperatures were equalised by direct transfer of heat between parts of the system, the final temperature would be $\frac{1}{2}(t_1 + t_1')$.

If the system consists of two quantities of gas at different temperatures, this calculation of the amount of work that may be done is applicable provided that each quantity of gas is kept at constant volume.

Digitized by Google

CHAPTER VII

ANY NUMBER OF INDEPENDENT VARIABLES

37. The number of independent quantities used to specify the state of a substance, at any given point of it, has been restricted to two. It is necessary now to shew how the theory of entropy, which has been established for this case, may be extended to the case of a substance which is such that the values of more than two quantities must be known in order to specify the state of any small portion of it*. The point to be noticed is that, whatever number of independent quantities the state of a substance may depend on, it is not necessary to vary more than two at a time in order to apply the argument by means of which the theory of entropy is derived from the second law of thermodynamics. The case of three independent variables is a simple one because it can be illustrated by geometry of three dimensions, but the same procedure applies to all cases.

An increase in the number of independent variables does not affect the properties of a reversible engine working between a source and sink of heat at given temperatures; nor the fact that a Carnot engine, in which the working substance performs a reversible cycle, consisting of alternate isothermal and adiabatic processes, is a reversible one. Thus all Carnot cycles that may be contrived, between two given temperatures, have the same efficiency; and this efficiency provides the definition of the thermodynamic scale of temperature. The complication, arising from the number of independent variables, comes in when we proceed to shew that $\int \frac{dQ}{t}$ is zero for any reversible cycle. This result follows from the possibility of obtaining the value of $\int \frac{dQ}{t}$ for any reversible cycle from the limiting case of a cycle made up of adiabatic and isothermal processes. An increase in the number of

* A solid elastic substance under conditions such that its stress must be specified by several independent components is an instance of such a substance.

Digitized by Google

independent variables greatly increases the variety of ways in which a given cycle can be obtained from one made up of adiabatic and isothermal processes, and a suitable way must be chosen in order that the argument which has been used may be applicable.

Let us take the case in which there are three independent variables, x, y, z. The temperature is a function of these if it is not itself one of them. If we regard x, y, z as rectangular coordinates, a given state of the substance is represented by a point in space, and a reversible process by a line. The first law of thermodynamics gives

$$dQ = dE + dW,$$

where E is a function of x, y, z; and, if the work is reversible, dW can be expressed in the form

$$Rdx + Sdy + Udz,$$

where R, S and U are functions of x, y, z, as in the case of two variables, see p. 18. Thus we have an equation of the form

$$dQ = Mdx + Ndy + Pdz,$$

where M, N and P are functions of x, y and z; and the equation satisfied by a reversible adiabatic process is

$$Mdx + Ndy + Pdz = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(1).$$

Suppose the equation satisfied by an isothermal process to be

$$\lambda dx + \mu dy + \nu dz = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(2).$$

This must be supposed to be known by experiment for any particular substance; it represents a system of isothermal surfaces.

Now take a given reversible cycle (not adiabatic). This is represented by a closed curve, or by two equations involving x, y and z. To deal with this cycle, let us take any surface (not isothermal) on which this curve lies, and confine our attention to processes represented by lines on this surface, distinguishing them as "permissible" processes. Equation (1) combined with the equation to the surface gives a system of permissible adiabatic processes; and equation (2) combined with the equation to the surface gives a system of permissible isothermal processes. These may be combined so as to form any number of permissible Carnot cycles, for each of which $\int\frac{dQ}{t}$ is zero; and the given cycle may be treated as the limit of a cycle composed of elements of permissible adiabatic and isothermal lines, in the same way as when we are dealing with a diagram in one plane. Thus we obtain the result that $\int\frac{dQ}{t}$ is zero for the given cycle.

Digitized by Google

Now consider all possible reversible processes by which the substance can pass from one given state to another. Any two of them may be combined so as to form a cycle for which $\int \frac{dQ}{t}$ is zero, therefore $\int \frac{dQ}{t}$ has the same value for all the processes. Consequently $\frac{dQ}{t}$ is the differential of a function of the variables. This function is the entropy of the substance. Thus the second law of thermodynamics requires that the differential equation (1) should be derivable from an equation of the form $f(x, y, z) = \text{constant}$, and represent a system of surfaces, namely surfaces of constant entropy. This is not generally true for a differential equation of this form with more than two variables.

When there are more than three independent variables the same argument can be used. If there are n variables a given process is represented by $n-1$ equations, and we may adopt as permissible processes those which satisfy a set of $n-2$ of these equations. This set of equations together with the adiabatic equation (containing n terms) give the permissible adiabatic processes; and the same set together with the isothermal equation give the permissible isothermal processes. We may obtain all the permissible processes by variations of only two quantities; and we may use these as coordinates in a diagram in one plane, and represent the permissible processes by lines in this diagram.

Thus the equation

$$t\,d\phi = dE + dW,$$

in which dW represents reversible work, is not restricted to cases in which the state of a substance depends on only two independent quantities. But when there are more than two independent variables a reversible process, starting from a given state, can no longer be defined by a single condition.

CAMBRIDGE: PRINTED BY JOHN CLAY, M.A. AT THE UNIVERSITY PRESS.

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

14 DAY USE
TURN TO DESK FROM WHICH BORROWED
LOAN DEPT.
his book is due on the last date stamped below, or
on the date to which renewed.
Renewed books are subject to immediate recall.

12 May '65 M J

REC'D LD
REC'D LD
APR 28 '65 -10 PM

21A-60m-3,'65
(2336s10)476B

General Library
University of California
Berkeley

Digitized by Google

Gaylord
PAMPHLET BINDER
Syracuse, N. Y.
Stockton, Calif.

Digitized by Google

Digitized by Google